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Los Alamos
N A T I O N A L   L A B O R A T O R Y

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PREFACE

   This book evolved from a set of lectures presented in 1996, 1997, and 1998 to new technicians and technical staff members in the Chemical Science and Technology Division of the Los Alamos National Laboratory. The Laboratory at that time was embarking on a program whose goal was the recovery of plutonium components from warheads that were being removed from the nuclear weapon arsenal of the United States of America. A major part of this program was the conversion of the plutonium metal from the warheads into a more stable form, such as plutonium oxide, that could be stored safely or made into a commercial power reactor fuel. The shift in technology emphasis from production of weapon-grade plutonium metal to conversion of the metal into stable and commercially usable forms demanded an increased support base for the chemical analysis of the plutonium contents in the various stages of the conversion processes that were being developed.

   Therefore, for whatever conversion method to be selected, it was important to prepare for the analytical chemistry requirements that would be needed to support the new technologies for the plutonium conversion program. This preparation included a significant emphasis on the development of chemical analysis methods to characterize the plutonium metal—the input to the conversion process—as well as the purity of the product of the conversion process and the many side streams resulting from it. There was little question that the development of these analytical procedures would result in significantly different procedures than those used to characterize steps in the production of plutonium metal for weapon uses. It was anticipated that the research and development of the conversion process would require an increase in the number of analytical chemists.

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ABSTRACT

This book is intended as a laboratory reference background for the people who will enter the national laboratories and production facilities to support the large task of chemical analysis in the conversion process. There are very few educational facilities that teach the elementary chemistry of plutonium and its radioactive properties. It is necessary, therefore, for new workers in this field to learn about chemistry of plutonium by "hands-on" experience, supervised by trained scientists. Workers with little experience in the field of plutonium chemistry need quick and practical information for their further training. There are many books available on the chemistry and radiochemistry of plutonium, but most of these are written for the professional scientist as reference works and are not easily accessible as quick and practical information for workers with little experience. The book is intentionally small in order to provide fundamental, elementary information the new worker needs. More detailed information is available in the existing literature.

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NOMENCLATURE

1. <u>Element</u> - A collection of atoms with the same chemical properties. The naturally occurring elements in the earths crust range from hydrogen to uranium, with a few omissions that are caused by radioactive instability. The elements are numbered from 1 to 92; hydrogen is element 1 and uranium is element 92.

    <u>Transuranium Element</u> - An element with an atomic number greater than 92. These elements do not occur in the earth's crust.

2. <u>Isotope</u> - The atoms of an element that have the same mass number. Plutonium-239 denotes a collection of plutonium atoms with a mass number of 239; thus, plutonium-239 is an isotope of plutonium.

3. <u>Nuclide</u> - Any atom of any element with a particular mass number. For example, the nuclide produced by the decay of Pu-239 is U-235. Some use isotope and nuclide interchangeably; however, isotope refers to a particular element while nuclide refers to any element.

4. <u>Radioactive</u> - The attribute of instability shown by some nuclides when they decay to another nuclide. The decay process is accompanied by the emission of some form of radiation.

5. <u>Alpha Particle</u> - a helium nucleus with a positive charge of 2, one of the forms of radiation emitted by the decay of a radioactive nuclide.

6. <u>Beta Particle</u> - An electron (negative charge) emitted by the decay of a radioactive nuclide. A radioactive nuclide can decay by emitting either an alpha particle or a beta particle, but not by both at the same time.

7. <u>Gamma Ray</u> - Electromagnetic radiation (similar to x-rays) that usually accompanies alpha particle or beta particle emission in the decay of a radioactive nuclide.

8. <u>Half-life</u> - The time in which the atoms of a radioactive nuclide will decay to half their number. The half-life of plutonium-239 is 24,120 years. One gram of plutonium-239 will be one-half gram by the end of that time, and the other half gram will have formed uranium-235.

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PROLOGUE

EUROPE

The Vacuum Discharge Tube

It all started with the investigation of the passage of electricity through glass vacuum tubes. Many scientists in the middle of the nineteenth century followed such experiments. About 1870, William Crookes, a young English physicist, invented an improved form of the "vacuum discharge tube." In principle it was not much different than the modern fluorescent light tube, except that the Crookes glass tube had no fluorescent coating inside and operated on direct current rather than on alternating current. The Crookes tube was a glass cylinder, closed at each end and roughly pear-shaped, with a metal wire sealed through its walls at each end. Inside the glass tube, the wire at one end was attached to a small disk called the "cathode", and the wire at the other end was attached to a metal plate called the "anode". The anode could be made in various shapes. When the tube had been evacuated of air and sealed off to preserve the vacuum inside it, the two external wires could be connected to a source of relatively high voltage supplied by a battery or an induction coil.

The making of the Crookes tube was the first step leading to the discovery of radioactivity. This and subsequent steps followed a classical chain of events, typical of the early revolutionary discoveries in science. The discovery of radioactivity was built on the invention and development of instruments and principles announced by scientists many years before radioactivity was discovered, and as was usual in

nineteenth century science, each of these developments resulted from the experiments of one person. An unusual fact is that the name "radioactivity" was not applied to the phenomenon by its discoverer but by a worker in the field two years after the discovery.

Operation of this vacuum discharge tube, the forerunner of the modern "cathode ray tube" or CRT, was simple. The electrical source of direct current voltage was connected to the two electrodes, with the negative side of the source being connected to the cathode, and the positive side of the source being connected to the anode. Various phenomena could be observed when the tube was operating, depending on the degree of vacuum in the tube, or in other words, how completely the air had been removed from the tube by the vacuum pump. As the air pressure within the tube was reduced and the tube was operated in a darkened room, the tube showed a series of luminescent bands between the cathode and the anode. As the air pressure was reduced to a higher degree of vacuum, the luminescent bands became closer together until they finally disappeared and there was only a dark space, known as the Crookes Dark Space, between the two electrodes. But two other effects appeared: (1) there was a glow around the cathode, and (2) a luminescence appeared on the walls of the glass tube in the vicinity of the anode. If the anode and cathode were in line along the length of the tube, and the anode was in the shape of a cross or some other geometrical shape, a sharp shadow image of the anode appeared in the luminous wall behind the anode. Investigators also found that a magnet, placed near to the tube between the cathode and anode, caused the luminescent area to move about, as if the "rays" from the cathode were being controlled in their

direction by the magnet. This effect resulted in naming the apparent stream of electricity between the cathode and anode, as "cathode rays". Later studies showed the cathode rays to be electrons emitted by the cathode.

The Discovery of X-rays

In 1895, Wilhelm Roentgen, a German physicist, was investigating the properties of the fluorescence formed on the walls of the Crookes tube. He had become interested in reports from other scientists that photographic plates still in their shipping containers became darkened if they were nearby a Crookes tube in operation. He found that even if the Crookes tube was wrapped in black paper and the photographic plate was placed in a black cardboard box, the photographic plate was still blackened by operation of the Crookes tube. Further experiments by Roentgen showed that the blackening was not affected by placing an aluminum metal plate or a copper metal plate between the tube and the photographic plate. He then found that the rays from the tube would go through other substances, including human flesh, and made the first x-ray photograph of the bones in a human hand.

Roentgen reported his results in December 1895, causing great excitement around the world. He won the Nobel Prize in physics in 1901, the first year Nobel prizes were awarded, for his discovery of x-rays.

The Discovery of Radioactivity

In January 1896, one month after Roentgen announced the discovery of x-rays, Henri Becquerel, a French physicist, heard a lecture on x-rays at the Academy of Science in Paris. Like his father and grandfather, he had always been interested in the fluorescence of certain materials following their exposure to light, and he wondered if there was a connection between this fluorescence and x-rays. He devised a set of experiments to see if the fluorescence observed by his father and grandfather in uranium compounds was related to x-rays.

Becquerel used the same batch of potassium uranyl sulfate that had been used by his father. His object was to see if exposure of the uranium compound to sunlight would excite fluorescent rays that would pass through black paper and create an image on a photographic plate. His method was to place crystals of the uranium compound in sunlight for most of the day, then wrap them in black paper and place the package in a light-tight box next to an unexposed photographic plate. He found that, indeed, the photographic plates showed a blackening following this procedure. On the last two days of February 1896, however, there was very little sunlight and he decided to save the materials for an experiment on March 1. To save time, he placed the wrapped crystals and photographic plates in the light-tight boxes in preparation for the experiments the next day. March 1 turned out to be cloudy, also, so he decided to proceed to develop the plates, expecting very little darkening. He was amazed to find that the darkening on the plates was as great as that from experiments on sunny days. In other words, although the fluorescence shown by the uranium materials was much dimmer on cloudy days than on sunny days, the darkening of the photographic plates was the same. Rays of some kind were being generated in the potassium uranyl sulfate crystals that seemed to be unrelated to exposure of the crystals to light.

Becquerel found that other uranium compounds had the same effect. They all emanated rays that could pass through dark paper and blacken a photographic plate. But unlike x-rays, no electrical discharge tube was required. He was surprised when he compared the amount of radiation from uranium-containing chemicals, such as the potassium uranyl sulfate, with the amount of radiation from unpurified uranium ores. He found that the ores gave off much more radiation than the pure compounds, suggesting that uranium was not the only element responsible for radiation in the unpurified ores. These results were first reported in February 1896.

Becquerel's findings attracted the attention of Marie and Pierre Curie, also working in Paris. In 1898 they concluded that the effect discovered by Becquerel was an atomic phenomenon not related to the chemical or physical form of the uranium compounds or the unpurified uranium ores. They made the first quantitative measurements of the amount of radiation by using a device that applied a voltage to a quartz crystal to generate a current that balanced the current coming from an ionization chamber containing the radioactive material. Using this method of measurement, they devised a series of laborious chemical separations to isolate non-uranium radioactivity from large amounts of pitchblende, an uranium ore, and

named the new radioactive element "polonium" in honor of Marie's native land, Poland. They were able to accumulate enough polonium to determine its atomic weight as 210.

Becquerel and the Curies shared the Nobel Prize in physics in 1903 for their work in the early days of the investigation of radioactivity. The Curies continued to work on the isolation of other radioactive elements from uranium and thorium ores and isolated 100 mg. of radium chloride from two tons of pitchblende in 1903. At this time they suggested the term "radioactivity" to describe the process discovered by Becquerel. After the death of her husband Pierre in 1906, Marie received a second Nobel Prize in 1911, this time in chemistry, for the discovery of polonium and radium.

Also in 1903, Ernest Rutherford and Frederick Soddy in England, who were studying this new radiation, postulated that it was the result of fundamental transformations in the atomic nucleus that led to the change of one element into another element. They discovered three types of radiation, which they named "alpha, beta, and gamma activity". Rutherford received the 1908 Nobel Prize in chemistry for this work and for his characterization of radon, a radioactive gas produced by the radioactive decay of radium.

The Discovery of the Neutron and the Fission Process

During the next thirty years the study of the naturally occurring radioactive elements from the radioactive decay of thorium and uranium became an active field for both chemists and physicists. These endeavors led to the beginning of the modern model for the atom, based on knowledge of the electron and the proton. Researchers realized that the model was incomplete, and in 1922 Rutherford postulated the existence of a neutral atomic particle similar in mass to the proton. In 1932 James Chadwick, also of England, discovered the existence of the neutron, thus completing the ideas of the structure of the atomic nucleus, which was to play such an essential role in the development of atomic energy ten years later. Chadwick received the Nobel Prize in Physics for this discovery in 1935.

Aided by the discovery of the neutron and ways to produce it, advances in the study of atomic reactions accelerated. In 1934, Enrico Fermi was working in Italy with the production of artificial radioactivity by neutron bombarding, "likely candidate materials" reported the production of beta particle activity when he bombarded uranium materials with neutrons. He speculated that the beta particles might be from element 93, the element expected if uranium were to absorb a neutron. He did not follow up on this observation with any chemical separations to identify the beta activity, which may have been beta particles from the fission products of uranium, but he continued to work with the effects of neutrons on other materials. He received the Nobel Prize in physics in 1938 for his use of neutrons in producing new radioactive elements.

Later in 1934 Id Noddack of Germany suggested that Fermi's element 93 might actually have been radioactivity resulting from splitting the uranium atom into two large fragments, and that these fragments could have been radioactive isotopes of known elements. Her comment, published in a technical journal, apparently received little attention.

It took four more years to solve the mystery of Fermi's unknown beta particle activity. In the fall of 1938, two German radiochemists, Otto Hahn and Fritz Strassmann, were attempting to identify the radioactivity resulting from neutron bombardment of uranium. They employed chemical separations that depended on the use of stable elements, whose chemistry was well understood, to act as "carriers" for the extremely small amounts of unidentified radioactive elements produced by the neutron bombardment. Because some of the activity was precipitated along with insoluble barium sulfate, they believed that the radioactivity was a new isotope of radium, whose chemistry would be expected to be similar to that of barium. They realized that this interpretation was on shaky ground because it required the unlikely emission of two alpha particles from the neutron-activated uranium nucleus. About the same time, Irene Joliot-Curie and P. Savitch, working together in France and also investigating the beta activity from neutron-bombarded uranium, chemically isolated activity with a 3.5-hour half-life, which they called "R 3.5 hr". Hahn had thought this was an isotope of actinium, which would be produced by the beta decay of his presumed radium isotope. Joliot-Curie and Savitch, however, found that in chemical separations "R 3.5 hr." followed lanthanum rather than actinium. They thought it could

be separated from lanthanum but did not demonstrate this. In fact the R 3.5 hr. activity later turned out to be lanthanum-141, a fission product. When news that the activity was separated by lanthanum or by actinium reached Hahn and Strassmann, they thought the French scientists were "very muddled up". The realized, however, that if the activity really was lanthanum, then it must be a decay product from barium, and proceeded with more experiments to solve the mystery.

January 1939—The Month of Discovery

These puzzling discoveries all came into focus shortly after New Years Day, 1939. In their new experiments, Hahn and Strassmann had found that the activity they had previously identified as a radium isotope could be separated from radium, but not from barium. They reported these results in the January 6, 1939 issue of *Naturwissenschaften*, a German scientific journal, saying that as chemists they believed their results, but as nuclear physicists they were reluctant to accept the implications since the results contradicted current nuclear knowledge. They had also noted that another activity, which they thought might be a heavier element in the rhenium family, might instead be a lighter rhenium homologue, which would make it element 43. They pointed out that the sums of the masses of this element and the barium they had identified added up to the mass of the uranium atom. They were still reluctant to commit to the "fact" of fission.

Ten days later, January 16, 1939, Lisa Meitner, a former colleague of Hahn's who had fled to Sweden from Nazi Germany, and her nephew Otto Frisch proposed an explanation for the German chemists' findings. They sent a letter to *Nature*, the British weekly science journal, suggesting that the only rational interpretation of the data was that the uranium atom was relatively unstable, and split into two approximately equal parts by the absorption of a neutron. They also proposed naming such a process "nuclear fission". They also noted that fission should be accompanied by large energy releases. On the same day, Frisch observed the large energy releases in an ionization chamber and reported these findings separately to *Nature*. The chemical evidence discovered by Hahn and Strassmann, the physical interpretation of this evidence by Meitner and Frisch, plus the direct observation of the energy released by fission thus established the reality of nuclear fission.

On January 26, 1939, Niels Bohr announced these results at a theoretical physics conference in Washington, DC. Before the end of January 1939, fission of uranium had been observed in ionization chambers in many physics laboratories in Europe, England, and the United States. Nuclear fission was a fact, and the race for the development of atomic energy in the United States was on. Otto Hahn received the 1944 Nobel Prize in chemistry for his work that had led to the discovery of fission. Niels Bohr nominated Meitner in 1946 for the Nobel Prize in physics, but the Swedish Academy of Science declined to endorse the nomination. In 1961, however, the Enrico Fermi prize was awarded to Strassmann, Meitner, and Frisch for their contributions.

AMERICA

Bohr's Announcement in Washington, January 1939

Meitner and Frisch had told Niels Bohr, the Danish physicist who was awarded the Nobel prize for physics in 1922, about their conception of the phenomenon of fission just before he made a visit to the United States in January. At a theoretical physics meeting in Washington on January 26, 1939, Bohr told the audience of physicists about the recent European discoveries. By the time the report of Frisch's detection of fission fragments was published in February 1939, half a dozen institutions in the United States, including the University of California, had conducted experiments that confirmed Frisch's results. The quest began for a detailed explanation of the fission process and, additionally, for the discovery of new elements beyond uranium—the transuranium elements.

The First Transuranium Element

In 1939 Edwin McMillan, at the University of California in Berkeley, observed a radioactive substance that emitted beta particles with a half-life of 23 minutes, following the exposure of a thin film of uranium oxide to slow neutrons. This was probably the same activity found by Hahn, Meitner, and Strassmann in some of their earlier experiments in 1936, but not identified by them. McMillan, however, made the additional discovery that another beta emitter with a half-life of 2.3 days grew into the 23-minute substance at a rate proportional to the decay of the 23-minute beta activity. Neither of these beta activities displayed recoil from the uranium oxide layer, which indicated they were not fission products. In collaboration with Philip Abelson, McMillan was able to identify the 23-minute activity chemically as U-239, produced by the neutron absorption of natural uranium-238, and the 2.3-day beta activity as element 93, the first element beyond uranium, element 92. He later named it neptunium.

McMillan and Abelson realized that the neptunium-239 must decay into element 94 because of its beta activity but were not able to find element 94 in their experiments, which were reported in May 1940. As it turned out later, the half-life of the expected element 94 was so long, compared to that of Np-239, that the amount of element 94 was too small to be detected. Later that year, in December, Glenn Seaborg, McMillan, and Joseph Kennedy, together with graduate student Arthur Wahl, isolated another isotope of neptunium, Np-238, following the deuteron bombardment of uranium-238. These findings were reported to the *Physical Review*, January 28, 1941, but publication was delayed until 1946.

The Path to Plutonium

In March of 1941 the first plutonium isotope to be discovered was plutonium-238. This came about following the production in early 1941 of additional amounts of neptunium-238, which permitted Seaborg, Kennedy, and Wahl to isolate element 94 from the neptunium-238. Working with trace amounts of the element, they were able to identify it as a new element, which they named plutonium.

Near the end of March 1941, Kennedy, Seaborg, Emilio Segré, and Wahl reported measurements made on a different isotope of plutonium, Pu-239. This isotope was

produced by irradiating 1.2 kilograms of uranyl nitrate for two days with neutrons from the beryllium target of the 60-inch cyclotron. The researchers separated 0.5 microgram of plutonium from 1200 grams of the uranyl nitrate. They estimated its half-life at about 30,000 years and found that it was even more fissionable than uranium-235. This discovery showed the feasibility of creating large amounts of plutonium for weapon purposes if nuclear reactors could be built for the neutron irradiation of tons of uranium. McMillan and Seaborg shared the 1951 Nobel Prize in chemistry for their discovery of the first two transuranium elements. Kennedy and Wahl went to Los Alamos in 1943, where they became leaders in the study of plutonium chemistry and production of the metal for its use in atomic bombs.

The First Man-made Nuclear Reactor

The feasibility of building a nuclear reactor for neutron production was demonstrated in December 1942, when Enrico Fermi, then at the University of Chicago, achieved the first nuclear chain reaction in a structure of graphite blocks and highly purified uranium oxide bricks. Fermi and his co-workers built this "pile" by hand. They constructed a stack of graphite bricks and uranium metal or oxide lumps in a carefully prearranged design. The graphite bricks were required to slow neutrons from the fission process in uranium-235 to low energies, which could be more easily absorbed by more uranium-235 atoms that would fission and produce even more neutrons. This would eventually lead to a nuclear chain reaction in which as many neutrons were being produced as were lost by escape to the exterior of the stack or by absorption by uranium and impurities. This

stack was called the Chicago pile because it resembled an orderly pile of brick. After each layer was put in place, the neutron count was checked to see how close the pile was to a self-sustaining chain reaction. On December 2, 1941, they placed the additional materials that theoretically would come close to producing a self-sustaining chain reaction. The neutron count then rose sharply when cadmium metal control strips (cadmium is a good absorber for neutrons) were partially removed and then leveled off at a constant value, indicating that Fermi and his co-workers had achieved the first man-made nuclear reactor. The pile was operated for a short time at a power of about 1/2-watt, then increased to about 200 watts on December 12. There was no radiation shielding for this first reactor, and continued operation would have subjected the scientists to excessive radiation exposure. For that reason it was dismantled and later rebuilt with proper shielding at Argon, Illinois, outside of Chicago, at a site to be known later as the Argonne National Laboratory. Fermi later came to Los Alamos after it was started in 1943.

Plutonium Production Reactors

The first prototype production reactor was built at Oak Ridge as a pilot design for the full-size production reactors later built at Hanford, Washington. Formally called the X-10 reactor, it was nicknamed the Clinton Reactor and started up in November 1943. It first operated at a power of 800 kilowatts, which was later increased to 2000 kilowatts. It initially had a production capacity of several grams of plutonium per month, and this later increased to several grams per day. Milligram quantities of plutonium were first shipped to Los Alamos in January 1944, and two months later Los Alamos was receiving

gram quantities. Until then the only source of plutonium for the Los Alamos scientists to study had come in microgram amounts from production in the cyclotron at Washington University in St. Louis. Early in January 1945, Los Alamos received a shipment of "Clinton" plutonium. This was used to produce two 0.9-inch-diameter metal hemispheres, each weighing 60 grams, for nuclear measurements. This first production of more than 100 grams of metal was the crucial test for the purification chemistry process developed by Wahl, and for the reduction of the purified plutonium fluoride to metal in the process designed by Richard D. Baker. This plutonium was isotopically the purest Pu-239 made in a reactor. The plutonium from the Hanford (WA) reactors contained appreciable amounts of Pu-240, a consequence of operating the reactors for longer periods of time before removing the plutonium from the uranium fuel rods.

Large-scale production of plutonium commenced in December 1944 after the reactors at Hanford were completed and started up in September. Initially there were two production reactors operating at a power level of 500 megawatts (MW), which ultimately had a production capacity of 500 grams of plutonium per day. This plutonium was not instantly available for Los Alamos. Production economics required that the uranium fuel elements had to remain in the reactors for a period of time to build up plutonium concentrations that could be economically separated from the uranium and the fission products produced by the nuclear reactions. The early yields of plutonium from the uranium in the reactors were less than 200 grams of plutonium for each million grams (one metric ton) of

uranium. The chemical separation process to isolate the plutonium in a pure form as plutonium nitrate was one of the most challenging problems of the atomic bomb project in America because the design of the process and the needed equipment had to be founded on milligram-scale experiments and equipment. There was no time to build an experimental, small-scale pilot plant.

The first delivery of Hanford plutonium was received in Los Alamos in February 1945, and this was an 80-gram batch. By March, multi-hundred gram batches were coming in from Hanford. By the summer of 1945 there was sufficient metal for use in the first full-scale test of an atomic bomb at Trinity Site near Alamogordo, New Mexico, on July 16. This was the only test before the first wartime use of a plutonium nuclear weapon. Japan surrendered unconditionally after two nuclear weapons were used by the United States over Hiroshima and Nagasaki on August 6 and August 10, 1945. The nuclear material in the Hiroshima bomb was U-235, while the nuclear material in the Alamogordo test and the Nagasaki bomb was plutonium.

Plutonium from a Natural Reactor

In 1975, an analytical chemist at a French uranium mine near the town of Oklo in Gabon, Africa, was examining the isotopic mass ratios for uranium taken from new batches of ores before they were shipped for use in the French atomic power industry. He noticed that the mass ratio of uranium-235, the fissionable isotope of uranium, was reported as 0.6%, which normally should have been 0.72%. Further investigation

revealed that this was not an error in the analysis, but was a valid number, and that furthermore, isotopic mass ratios of samples close to the mine location of this first sample, showed similar and abnormally low values for the uranium-235 mass ratio to the total uranium.

The chemists began looking at mass ratios in other elements in these ore samples. They found abnormalities, which could only be explained by the fission of uranium-235, in the mass ratios of elements. Using this isotopic mass ratio data, the mine operators discovered that they could construct a map showing an area about 30 meters wide and about as deep, in which they could find abnormal mass ratios. Other uranium mining sites in the vicinity showed normal mass ratios for uranium and the other elements that included stable fission product isotopes.

This discovery led to the supposition that nearly two billion years ago, natural circumstances created a concentration of uranium materials at this location that resulted in a sustained nuclear fission chain reaction. At that time in the earth's history, the abundance of uranium-235 was about 3%, instead of the 0.72% that is found today, since uranium-235 has a decay rate that is about seven times that of uranium-238, the only other naturally occurring uranium isotope of significance. This natural reactor probably persisted for somewhere between 200,000 and 500,000 years, at a low average power of 20 kilowatts. Over its lifetime it consumed about six tons of uranium, enough to fuel a modern power reactor for about four years. It also undoubtedly produced plutonium-239, most of which would have decayed back to uranium-235, in what was possibly the first breeder reactor on Earth.

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CHAPTER 1

DISCOVERY OF PLUTONIUM

After the announcement of the discovery of the fission of uranium in early 1939, scientists in Europe and America commenced the search for the elements beyond uranium. The first of these would be produced not by fission, but by the absorption of a neutron by uranium-238, followed by beta particle emission from the newly formed uranium-239. Other reactions were also possible, such as bombardment with deuterons instead of neutrons.

Edwin McMillan and Philip Abelson published the announcement of the discovery of element 93 in *Physical Review*, the American physics journal, in May 1940. They chemically isolated a beta particle emitter with a 2.3-day half-life from the 23-minute U-239 activity. Their further chemical experiments demonstrated that the new activity was element 93. The new substance was later named neptunium, after the planet Neptune that lies beyond the planet Uranus. Since it was a beta particle emitter, they knew its decay product must be element 94 but were unable to find any traces of that element, probably because not enough element 94 was being formed to allow detection of it.

Work continued on the search for element 94 during 1940, but publication of further scientific results was voluntarily postponed because the scientists felt that the investigations could lead to extraordinary applications of nuclear energy for war purposes. Scientists at the University of California at Berkeley, under the leadership of Glenn T. Seaborg, a chemist, formed teams to combine both physics and chemistry in the discovery of element 94.

In December 1940, Seaborg, McMillan, Joseph Kennedy and Arthur Wahl, all chemists, produced another neptunium isotope, with a mass of 238, by bombarding uranium with deuterons. After isolating the neptunium-238, they noted that alpha-particle activity was growing in it as it decayed. Further work during the early part of 1941 confirmed that this new alpha-active substance was element 94, with a mass number of 238, which they later named plutonium, for the planet Pluto, which lies beyond Neptune. This work was reported to the *Physical Review* in January and March of 1941, but not published.

On March 29, 1941, Kennedy, Seaborg, Emilio Segré and Wahl reported on work that produced the first plutonium-239. They produced it by irradiating 1.2 kilograms of uranyl nitrate with neutrons for two days, using neutrons from the beryllium target of the Berkeley 60-inch cyclotron. This irradiation produced neptunium-239, which they chemically isolated from the uranium. The neptunium decayed into plutonium-239, yielding a total of 0.5 microgram of that isotope. They found that it was more fissionable than uranium-235 and estimated its half-life to be about 30,000 years. This work defined the way that the production reactors at Hanford, mentioned above, would produce large amounts of plutonium, by neutron irradiation of uranium-238. Kennedy and Wahl were invited by J. Robert Oppenheimer, the director of the new atomic bomb project at Los Alamos, New Mexico in 1943, to participate in the work needed to produce plutonium metal for the nuclear weapon components.

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CHAPTER 2

THE MAKING OF PLUTONIUM

Plutonium is by far the most important element in the actinide series because of its value for the production of large amounts of energy, both for weapons and for fuel in commercial power reactors. The plutonium, which is the subject of this book, is the kind common to weapon programs at Los Alamos and is sometimes called weapon-grade plutonium.

The element plutonium, whose chemical symbol is Pu, is element 94 in the periodic table. It shares similar but not identical chemical properties with a group of elements known as the actinide group, whose first member is actinium, element 91. As in the lanthanide, or rare earth group, each higher element differs from its lower adjacent neighbor element by having a new orbital electron placed in an inner orbit, instead of the most external orbit. This confers similar, but not identical, chemical properties to the elements in the actinide series. Only the first two elements in the actinide series, actinium and uranium, are found in nature.

Weapon-grade plutonium in quantity was first made in the Hanford reactors, and later in reactors at Savannah River, Georgia. As explained above, it is made by the absorption of a neutron in uranium-238, producing uranium-239, which quickly decays to neptunium-239, which decays in a few days to plutonium-239, which has a long half-life of 24,120 years. All of this takes place in the uranium fuel rod in the reactor.

In order to make the extraction of the plutonium from the uranium fuel rod economically feasible, the fuel rod remains in the reactor until the plutonium

concentration builds up to somewhere around 600 grams per 1,000,000 grams of uranium, or about 600 parts per million. During this time other nuclear processes are occurring in the plutonium and the uranium. One thing that occurs is that the plutonium-239 absorbs a neutron, and this creates a small amount of plutonium-240, which in turn can absorb a neutron to produce plutonium-241, which in turn can absorb a neutron to form plutonium-242. All of these plutonium isotopes have half-lives between 14 and 375,000 years. Because the half-life of plutonium-243 is only 5 hours, this isotope does not accumulate in the fuel rod; the heavier isotope build-up stops at plutonium-242. One other isotope is produced, plutonium-238, by the emission of two neutrons from the uranium-238 nucleus, producing neptunium-237. This nuclide can absorb a neutron to become neptunium-238, which quickly decays by beta-particle emission to plutonium-238. The list of plutonium isotopes made in the production of weapon-grade plutonium is shown in Table 2-1, along with their nominal abundance in terms of weight-percent.

Table 2-1.
Nominal Composition of Weapon-Grade Plutonium

Isotope	Abundance, wt-%	Half=Life, yr.
Pu-238	0.008	87.7
Pu-239	93.7	24,120
Pu-240	6	6,570
Pu-241	0.3	14.3
Pu-242	0.005	375,000

The index for the suitability of reactor-produced plutonium for use as weapon-grade plutonium is the percentage of plutonium-240 in the mixture of isotopes. Plutonium-240 has a higher spontaneous

fission probability than does plutonium-239, and too high a percentage of plutonium-240 can cause a weapon's explosive efficiency to be lower than desired. Reactor engineers sometimes refer to plutonium that contains much more than 6% plutonium-240 as reactor-grade plutonium or "dirty" plutonium, mainly suitable for fueling commercial power reactors. The 6% value is not a rigid guideline since a considerable amount of weapon-grade plutonium produced in the 1950s contained as low as 2% plutonium-240, but this plutonium was more costly to produce on a dollar-per-gram basis.

Much of the cost of production of plutonium is caused by the difficulty of extracting the plutonium from the uranium fuel rod. When the fuel rod is removed from the production reactor, it must be allowed to cool for a number of weeks to give time for the short-lived fission products to decay to a level that permits handling and chemical processing of the fuel rod. After this cooling period, the fuel rod and its protective metal cladding are dissolved in acid, and the plutonium, which comprises only 0.06% or less of the total uranium weight, is separated from the dissolved cladding, uranium, and remaining fission products by complex and carefully controlled chemical separation steps. Since 1945 these chemical separation processes, some of which are no longer used, have been based on three main types of separation techniques: (1) bismuth phosphate carrier precipitation, related to the carrier techniques used by the Curies at the beginning of the twentieth century, (2) liquid extraction processes such as the use of tributyl phosphate/kerosene extraction from

the acid dissolver solution, and
(3) ion-exchange column methods to concentrate the plutonium on ion exchange beads. The final product is a concentrated plutonium nitrate solution, free of fission products but still containing small amounts of stable element impurities such as iron and aluminum.

This concentrated plutonium nitrate, containing about 300 grams per liter of plutonium must be processed to remove impurities and then converted to high-purity metal for weapon use. It is especially important to eliminate the light elements below sulfur because these could undergo nuclear reactions with the alpha particles from the plutonium that would produce an undesirable neutron background. This undesirable reaction can lead to low explosive efficiencies in a nuclear weapon. The final product from these steps was usually plutonium tetrafluoride, which was then reduced to metal with calcium and iodine at high temperature. The purity of the final metal was critical because any fluorine remaining in it would contribute to an undesirable neutron background.

The pure metal made in this way is extremely hard and difficult to machine to the shapes needed for use in a weapon. It is very heavy, weighing almost 20 grams per cubic centimeter. It is alloyed with a small amount of gallium, a metal whose melting point is 29.8ºC, to make it more easily machinable. This alloy permits a high-temperature metallic phase of plutonium metal to remain stable at room temperature, and this phase is a little less dense than the pure metal and lends itself to machining operations.

In all operations where work is being done with plutonium metal, it must be protected from the atmosphere, whose water vapor reacts with the metal to form an ever-thickening layer of plutonium oxide on its surface. The handling of plutonium metal is done in moisture-free, inert atmospheres, usually argon. In order to protect the metal from atmospheric moisture when it must be handled in the open, it can be protected with a thin layer of nickel metal. This coating also prevents the removal of alpha-particle contamination, so that the plated metal items can be handled with bare hands.

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CHAPTER 3

SAFETY AND HAZARDS WITH PLUTONIUM MATERIALS

Plutonium is a toxic substance, but it is not "the most toxic element in the world". This statement is frequently uttered by those not well acquainted with its properties and is seen in the news media. There are many substances in modern chemical and pharmaceutical industries that are more dangerous to handle than plutonium, and there are many natural toxins that are more toxic on a gram-to-gram basis. In addition, there is no scientifically or medically supported occurrence of a human death from the ingestion or inhalation of plutonium materials during more than fifty years of handling plutonium materials in this country. This safety record stems from the precautions adopted by authorities that managed plutonium research and processing from its very first discovery. This does not include the three deaths that have occurred from the release of radiation during accidental fissioning caused by critical excursions of kilogram quantities of plutonium, which are described in a later section of this chapter.

Work with plutonium materials, nevertheless, can create hazardous situations in the laboratory when simple safety rules are not observed. The operations in an analytical chemistry laboratory deal mainly with plutonium in quantities less than a gram and are performed in specially ventilated enclosures, designed to contain the radioactive material if a spill occurs. Hazardous situations can be prevented by using the basic rules of good chemical laboratory practices and using the proper safety procedures. Most hazardous situations result from carelessness or inattention to

these practices and procedures. Hazardous situations that do occur can be controlled and confined with relative ease because plutonium's alpha particle activity makes it easily detectable.

It is important to consider that knowledge of either the chemical effects or the radiation effects of plutonium in humans is sparse because there is very little information based on human experience. The few chemical workers who have accidentally ingested microgram amounts of plutonium have shown no clinical symptoms during the many years following their exposure. Most of our conjecture about the effects of plutonium in the human body has been extrapolated from animal experiments.

The Chemical Hazard

As a chemical element, aside from its radioactivity, plutonium, like lead, is a heavy-metal poison. The primary difference between plutonium and the other non-radioactive heavy metals is that its radiation effects would probably create a health hazard rather than any chemical effects in the long run, with the possible production of radiation-induced tumors.

The Radiation Hazard

The principal radiation from plutonium is the alpha emission. One milligram of plutonium emits approximately 150 million alpha particles per minute. The associated gamma ray emission from plutonium is negligible because the number of penetrating gamma rays is thousands of times smaller that the alpha particle emission rate. These alpha particles from an external source are stopped by the outer layers of the skin and do

not penetrate into the deeper living cells of the skin, the dermis, the living layer of the skin. The only danger from alpha particles occurs when plutonium is swallowed, inhaled, or enters the bloodstream through a laceration, cut, or bleeding scratch. Thus, exposure of laboratory workers to external radiation from small amounts of plutonium is not hazardous.

Plutonium inside the body, however, in amounts greater than several micrograms, can create a health hazard. The introduction of plutonium into the human body would produce a delayed and long-term health hazard, which could ultimately lead to death, probably from the formation of malignant tumors. There are practically no data on such an outcome. In the years since plutonium research and use was started in 1941, the danger of ingestion of plutonium has been recognized, and safety measures were instituted from the very beginning to prevent introduction of plutonium into the body. Several accidents that caused internal exposures have occurred during the history of operations at Los Alamos, but up to the writing of this primer (1997) there has been no medically or scientifically documented instance of an illness or death from these accidents, which involved only micrograms of plutonium. Neither is there any proof of ill effects occurring in Los Alamos plutonium workers, either still working, retired, or deceased. The procedures to protect plutonium workers have been remarkably effective during this period of more than fifty years.

The former standard for plutonium accumulated in the body was 0.4 microgram. This is equivalent to about 70,000 alpha particles per minute. This standard was derived from measurements of the effects of plutonium deposited in animals and is based on radiation hazard and not on chemical toxicity. There are a few individuals, less than twenty altogether, who incurred body burdens of several micrograms during the early work with plutonium during World War II. They have not developed any health symptoms directly traceable to the plutonium in their bodies. Most of these individuals are now in their eighth decade of life. The amount of 0.4 microgram of plutonium, producing 70,000 alpha particles per minute, is also equivalent to 22 nanocuries, a unit that is used by radiation protection workers to express the amount of radioactivity present in a material. This unit is derived from the curie, which is defined as 3.7×10^{10} disintegrations per second, the amount of radioactivity in a gram of pure radium, and was so named in honor of Marie Curie, the discoverer of the element radium.

There are three main routes for the introduction of plutonium into the body: (1) through the mouth into the gastro-intestinal tract, (2) by inhalation into the lungs, and (3) by cutting or puncturing the skin with a plutonium-contaminated object so that plutonium gets into the blood stream. To prevent the first mode there is a rule that absolutely forbids the use of mouth pipettes for dispensing plutonium solutions and also a rule that absolutely forbids eating or drinking in plutonium laboratories. Wearing rubber gloves prevents getting the hands con-taminated with plutonium, which could later be transferred to the mouth. To prevent the second mode, all dry plutonium compounds, because they might produce dust, are handled only in closed or inert-atmosphere enclos-ures, usually called dryboxes. Working with these compounds in a fume hood or "open-front" enclosure is not permitted. The third mode is the most subtle and insidious because chemical apparatus of many kinds can cause injury resulting in a skin laceration

if careful practices are not followed. Thus, the prevention of intro-duction of plutonium into the blood-stream becomes a matter of learning how to use chemical tools and apparatus in a safe manner.

Consideration of the relative risk of the three modes of introduction leads to inhalation as the mode with the highest risk to health for a given amount of plutonium. This is because once plutonium is deposited in the lungs, the body's mechanisms for removing it are poor, and the lungs become a source of plutonium for distribution into the blood and other organs. Plutonium in the bloodstream can be removed by methods that bind the plutonium to certain injected chemicals, which are then excreted by the kidneys, but these methods must be started quickly to avoid deposition of the plutonium from the blood into the bones and major organs. None of the individuals treated in this manner have developed symptoms of the effects of radiation exposure. These complexing drugs are safe when given as recommended. Ingestion of plutonium ranks as the least risky because only very small amounts of the plutonium are absorbed into the bloodstream through the intestinal wall, and the remainder is eliminated through the bowels.

Plutonium Deposition in the Body

What is known about deposition of plutonium in the human body is very largely based on extensive experiments with animals, mainly rodents and dogs.

Plutonium that is deposited in the lungs is difficult to remove from the body. Once in the lungs it dissolves at a rate dependent on its chemical form and enters the bloodstream. Most of the plutonium in the bloodstream

will eventually deposit on the surface of bones and in the liver, with the bones receiving the larger part of the plutonium in the blood. It apparently remains in these sites for the life of the animal. Dogs with high exposures to plutonium from inhaling plutonium-bearing mist or by injection with plutonium show a high incidence of bone cancer tumors after a number of years from the time of their exposure to the plutonium. The tumors result from damage to the body tissue by the alpha particles emitted by the plutonium.

Plutonium that is accidentally ingested through the mouth, thus gaining entry to the gastro-intestinal system, is largely eliminated from the body in the feces. Animal measure-ments have shown that 0.003% of soluble plutonium that is in the +3 or +4 oxidation state, will be transferred through the intestines to the blood. If the plutonium is in the +5 or +6 oxidation state, the fraction that is transferred is 0.3%.

Specific Hazards

Solutions

Working with plutonium materials carries with it a certain degree of risk, as does work with many hazardous nonradioactive materials. The degree of risk is related to whether the plutonium material is in solution, whether it is the metal, or whether it is a dry compound.

There is no inhalation hazard from plutonium compounds dissolved in aqueous solutions. The dissolution procedure, however, may create a contaminated spray and must be performed in an approved enclosure. Plutonium compounds, except plutonium hexafluoride, which cannot be

handled in an aqueous solution, have no measurable vapor pressure above the solution, and hence no plutonium escapes from the solution into the air. This is a specific property of most chemical compounds in aqueous solutions. The only danger that exists with plutonium solutions is the risk of accidentally spilling them from their containers, and it is possible for the spilled solution to evaporate and leave a dry residue, which can become a dust and thus be airborne. For this reason, plutonium solutions that contain more than several hundred milligrams of plutonium should be handled at least in open-front enclosures. Plutonium solutions that contain less than 100 milligrams can be handled on laminar-flow-ventilated bench tops. The guiding principal here is how difficult would a cleanup be if part or all of the solution was spilled from the container, and what kind of containment is provided by the work space to prevent the spread of the spilled solution.

Solids

All solid plutonium compounds should be regarded as potential inhalation hazards because of the possibility that they can create dusts when manipulated in chemical operations. Therefore, they should be handled only in closed glove boxes. Containers of dry plutonium compounds should never be opened unless they are within a closed glove box. The only possible exception to this rule is pieces of plutonium metal that weigh more than several hundred milligrams. Ordinarily the metal will not form a dust unless it has been exposed to the atmosphere for a long enough time to enhance the formation of corrosion products on its surface as a result of reaction with the water vapor in the air. This could lead to

removable plutonium dioxide or plutonium hydride. Occasionally an analyst may encounter a plutonium metal piece that has been coated with a thin layer of nickel metal. Such pieces can be handled in an open air environment if they are free of radioactive contamination of their surfaces.

Gases

Plutonium hexafluoride, PuF_6, is a solid compound that has considerable vapor pressure at room temperature. Thus, it presents a significant inhalation hazard. Because it reacts violently with water at room temperature, it also is considered to be chemically hazardous.

Plutonium dioxide smoke can be formed when fine particles of plutonium metal are involved in a fire, whether from a pyrophoric reaction with air or from being involved in a fire in the laboratory. A plutonium dioxide smoke, although dense, can be mixed into the atmosphere through turbulence and thus become a significant inhalation hazard. Even if the smoke particles are small enough to be exhaled from the lungs, a dangerous fraction is likely to remain in the lungs.

Neutron Sources

A mixture of plutonium and beryllium metal or oxide is sometimes used as a neutron source in the radiochemistry laboratory. Such sources are usually sealed in doubly encapsulated tantalum containers that have non-radioactive external surfaces. Their construction is rugged, and they can be safely handled in an open air environment. Their neutron emission rate is ordinarily low enough that they do not present a radiation hazard.

Cleanup of Liquid Spills

Spills of dilute plutonium solution, whether located in a working enclosure or on the open benchtop or floor, should be cleaned up immediately. If the amount of plutonium in the spill is on the order of micrograms or milligrams, the liquid should be soaked up with laboratory paper towels until the area is dry. The area should be checked with a portable alpha particle monitor, and if alpha activity is detected, the area should be sprayed with a dilute solution of sodium ethylene diamine tetra-acetic acid (commercial FantaStik is also effective), and wiped dry. Very dilute nitric acid (0.1 $\underline{M}$) can also be effective, but hydrochloric acid should not be used, especially on stainless steel surfaces. The cleaning process should be repeated until no further activity is detectable. Rubber gloves must be worn, but a breathing mask is not required since the plutonium will not get into the air from a wet or damp surface. This cleanup procedure will be effective for most spills that occur in an analytical laboratory. If the spill involves more than several milligrams of plutonium, then the spill site should be wet down with water to insure that it does not dry out, and the chemical spill coordinator should be called for assistance. Remember that keeping a spill site wet prevents the plutonium from escaping into the air. Even spills that have dried but contain less than one or two micrograms of plutonium (more than 300,000 alpha counts per minute) will not release a detectable amount of plutonium into the air.

Critical Mass Hazard

The plutonium encountered in the analytical laboratory usually contains more than 90% of the isotope plutonium-239,

which is fissionable by neutrons. If large enough masses of plutonium are assembled together under the right conditions, a nuclear chain reaction will be initiated that will result in the very rapid emission of large amounts of neutrons and gamma rays. This kind of an event is known as a "criticality excursion" and is nearly always the result of the accidental assembly of the plutonium. It is differentiated from a "nuclear explosion" of the type created by an atomic weapon because it ordinarily is not physically destructive and terminates itself through the changes it causes in the nuclear material assembly within a matter of milliseconds. But in this short time the excursion can cause the emission of greater than 10^{15} neutrons and large amounts of gamma rays from the nuclear chain reaction involving the plutonium-239. This radiation from the criticality excursion can be lethal to individuals who are within a few feet of the nuclear material.

The amounts of plutonium involved in criticality excursions at Los Alamos have been greater than three kilograms in three excursions, which resulted in fatalities. Two of these occurred during the experimental measurement of neutron multiplication when two hemispheres of plutonium metal, together weighing about 6.2 kilograms, accidentally were moved into a configuration that caused the excursion. One of these incidents exposed only the experimenter, who was alone, and who immediately disassembled the critical configuration, while the other exposed the experimenter and several people in the room. Again the excursion was terminated by the experimenters, who disassembled the critical configuration immediately. In both accidents, the experimenter died of radiation damage to the body within a number of days. Those who were in the room during the second

accident received significant doses of radiation but survived. There were residual effects in one person.

The third criticality excursion occurred in a chemical processing plant where plutonium was recovered from various scrap materials that resulted from plutonium metal production. In this case the amount of plutonium was a little over three kilograms and was contained in an organic solvent solution. The stainless steel vessel that held this solution also held a dilute nitric acid solution that lay underneath the organic solution, which was lighter in density. The chemical technician conducting the chemical operations, and who believed that the plutonium had been previously removed from the organic solvent, mounted a step stool beside the vessel and pushed a switch to start the vessel's stirring paddle. Within less than 20 milliseconds there was a dull thud and a short flash of blue light from the sight port in the vessel. The operator shut off the stirrer, stepped down and complained that he was "burning up inside". He died within 40 hours from a massive exposure to neutrons and gamma rays. Another operator in the room about fifteen feet away suffered no ill effects although he received a significant dose of radiation. In this case, when the stirring paddle was started, it moved the dilute nitric acid solution up the inner walls of the vessel, surrounding the organic solution loaded with plutonium. The hydrogen in the water solution of nitric acid provided a very efficient neutron reflector for the small amount of neutrons always present

in plutonium materials. These neutrons, instead of escaping through the walls of the vessel, were reflected back into the organic solution. This led to a nuclear chain reaction and excursion that terminated itself in a fraction of a second. Even if the operator had not turned off the stirrer, the nuclear reaction would have terminated because of the dispersal of the water reflector when it became mixed with the organic solution.

These examples illustrate how unexpected circumstances can lead to a criticality excursion when handling kilogram amounts of plutonium. These accidents occurred in the late 1940s and 1950s, and since that time strict rules have been developed to prevent similar accidents. Although in an analytical laboratory it is very rare to be handling kilogram quantities of plutonium, the following rules for criticality safety have been in place since the chemical processing plant accident occurred in 1958. They are called "Ever Safe" conditions because if they are followed in an analytical chemistry or research laboratory, it is impossible to create a configuration of plutonium that will undergo a critical excursion. Other rules exist for other plutonium forms, but the following apply to plutonium solutions.

Ever Safe Conditions

a.   Mass - Less than 500 g Pu in a container

b.   Concentration - less than 10 g per liter

c.   Container size - less than 15 cm diameter

Any one of these conditions will prevent a critical excursion.

CHAPTER 4

PLUTONIUM METAL PREPARATION

The most widely used method to make plutonium metal is the "bomb reduction" method, which is named for the fact that it employs a sealed vessel, whose interior surface is lined with a high-temperature-resistant ceramic material, in which the reaction is carried out at high temperatures. This method was developed at Los Alamos in 1944 and has provided the basis for most of the nearly 90 metric tons of plutonium produced in the United States for weapon purposes. The method consists of reducing plutonium trifluoride with calcium metal by the reaction

$$2\,PuF_3 + 3\,Ca \rightarrow 2\,Pu + 3\,CaF_2, \qquad (4\text{-}1)$$
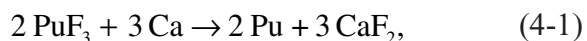
to which a small amount of iodine is added to increase the heat of the reaction. The slag containing the calcium fluoride and other impurities thus remains molten and allows the dense molten plutonium metal to settle to the bottom of the vessel, from which it can be recovered as a single button after the reaction is finished and the vessel is cooled to room temperature.

Plutonium metal can also be prepared in ultra-high purity form by the electro-refining method, developed at Los Alamos in the late 1960s. A direct current is passed through a molten bath of sodium and potassium fluoride, between a tantalum anode and an impure plutonium metal cathode made from plutonium metal scrap or plutonium metal from the bomb reduction process. The impure metal at the cathode dissolves in the molten salt bath under the influence of the direct current, and the plutonium ions migrate to the tantalum cathode where they are reduced to the ultra-pure metal. Because

of the shape of the electro-refining vessel, the plutonium is recovered as a doughnut-shaped ring. The process is more expensive than the bomb reduction process and requires as long as four days to produce a 400-gram metal ring.

A third preparation method is the direct oxide reduction process. This is an alternative to the bomb reduction method and gets its name from the fact that instead of making plutonium fluoride from plutonium oxide, the process omits the hydrofluorination step and uses the oxide as the feed material for the metal production. The process is carried out in a molten bath of calcium chloride. There is a tendency for the resulting metal to pick up impurities from the calcium chloride bath; therefore, this method can be used to produce metal as feed material for the electro-refining process.

Recently the lowest-recorded impurity levels for Pu have been reported [*Journal of Nuclear Materials*, **274**(3),315–319 (1999)]. Double-electron-refined metal was purified by a levitation method.

The electrical resistance of plutonium metal is among the highest for the metallic elements, being 145 microhm-centimeter at 300K. For comparison, resistivity of iron is 10, and that of copper is a little less than 2 microhm-centimeter.

Plutonium metal forms alloys with many different metals, including the gallium alloy discussed later. These other metals include aluminum, iron, cobalt, nickel, vanadium, chromium, and lead, to mention the more extensively studied systems. A ternary alloy with iron and cobalt has a melting point of 475 degrees, which is significantly lower than the 640 degree melting point of pure plutonium metal; this alloy was produced in

quantity a number of years ago as a candidate fuel for a proposed molten plutonium power reactor.

Some of the properties of plutonium metal are shown in Table 4-1. Plutonium metal has a silvery luster when newly made in an inert atmosphere free of water vapor. Like thorium and uranium it tarnishes fairly rapidly when exposed to the ordinary atmosphere, through reaction with the moisture in the air, and not so much from reaction with oxygen. This tarnishing, which is noticeable within a day's exposure, turns the metal's surface to a light bronze color that becomes darker until it is brown-black within a week or so. If left unchecked, the reaction will ultimately result in a green coating of plutonium dioxide.

Table 4-1.
Properties of Plutonium Metal

Density	g/cc19.8
Color	Silvery
Melting point	640ºC
Boiling point	3235ºC (from vapor pressure data)
Allotropic Forms	6

While plutonium is a very hard and dense metal like uranium, it is not very resistant to retaining its silvery luster when unprotected from air. Tarnishing which occurs at the surface of the metal, is thought to be

$$3Pu + 2H_2O \rightarrow PuO_2 + 2PuH_2. \qquad (4\text{-}2)$$
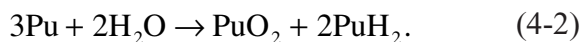
Both the oxide and the hydride in equation (4-2) are solids and will form a coating on the metal surface. In dry air (0% relative humidity) this reaction has a relative rate of 1. In air with a relative humidity of 50% the

reaction rate can be as high as 10,000. In argon that contains water vapor, but not oxygen, the rate is greater than 10, 000. Thus, it seems that the corrosion rate is controlled by the water content of the environment, and not by the oxygen content.

Plutonium metal has a great affinity for oxygen under certain conditions, even though the changes described above are mainly the result of reaction with water vapor. Finely divided metal particles, such as those produced by filing the metal, can be pyrophoric and spontaneously ignite to form a plutonium oxide smoke. The smoke can be extremely hazardous if inhaled because some of the plutonium will be deposited in the lungs, from which it can be transported by the blood to other organs of the body. Thus, the alpha radiation can cause severe cell damage or lead to the formation of malignant tumors, not only in the lungs but also in other parts of the body. Pyrophoric reactions do not occur with single pieces of plutonium metal that are large enough to prevent spontaneous ignition.

The metal is also attacked by gases such as ammonia, hydrogen, carbon dioxide, carbon monoxide, and all of the halogens. These reactions proceed fairly rapidly at elevated temperatures.

An unusual property of the metal is that it can exist in six allotropic forms, a property not found in most metals or non-metals. An example of allotropic forms in non-metals occurs in carbon, which exhibits three allotropic forms, commonly known as amorphous carbon black, graphite, and diamond. Each of the six allotropic forms of plutonium is different in its density and

hardness. The pure metal at room temperature has a density of 19.6 and is very hard and brittle. When it is slowly heated to its melting point at 646ºC, it experiences sudden, not gradual, changes in its density and ductility at definite and reproducible temperatures. Each abrupt change marks the formation of a different phase. All of these metallic phase changes result in an expansion of the metal (and a lower density), until the fourth phase—the delta phase—is reached at 375ºC. This phase has a density of 15.6 grams per cubic centimeter and is the least dense of the six phases. The fifth and sixth phases show slight increases in density up to the melting point. As the molten metal is cooled, it goes through these phase changes in reverse, until it returns to the room-temperature phase—the alpha phase. Adding a small amount of gallium to the metal when it is molten stabilizes the delta phase, and the metal remains in this phase when it returns to room temperature. The addition of gallium results in a form of plutonium metal that is much more easily machinable than the hard and brittle alpha phase.

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CHAPTER 5

DISSOLUTION OF PLUTONIUM MATERIALS

Metal and oxide are the most common plutonium materials that the analyst is given to dissolve before performing analysis. The metal samples are relatively easy to dissolve, while plutonium oxide (most usually plutonium dioxide) requires more effort. A third class consists of various plutonium compounds, most of which are easily soluble in dilute acids.

Metal

It is important for the plutonium chemist to be familiar with the reactions between plutonium metal and the various mineral acids since dissolution of the metal is the usual starting point for preparing plutonium solutions. Very few plutonium compounds are available for use in plutonium studies, and long-term changes take place in stored plutonium solutions owing to disproportionation and possible hydrolysis reactions, which will be described later.

Table 5-1 shows a list of common inorganic acids and their effects on dissolving plutonium metal. Plutonium metal, either the pure metal or the delta metal described earlier, dissolves most readily in hydrochloric or hydrobromic acid. The reaction is rapid and accompanied by evolution of hydrogen gas and heat. Common practice is to use 6 $\underline{M}$ HCl or to cover the metal with water and to add 12 $\underline{M}$ HCl slowly. Metal sample amounts rarely involve more than 100 milligrams, most usually 10 to 50 milligrams. By covering the metal first with water, then by

adding the 12 $\underline{M}$ acid slowly, the researcher can more easily control the reaction. If blue-green crystals of $PuCl_3$ are noticed, the researcher should add a small amount of water before adding more acid if the metal is not completely dissolved.

Table 5-1.
Dissolution of Plutonium Metal

Solvent	Effect
Water	Dissolves very slowly
HCl, HBr	Dissolves rapidly in 1:1 solutions
HF	Dissolves slowly in massive form, rapidly in turnings
HNO_3	No dissolution, unless trace of HF
H_2SO_4	Ordinarily slow dissolution
H_3PO_4	Dissolves in hot, concentrated acid

Hydrofluoric acid is only rarely used for the dissolution of plutonium metal. It is most effective on small, thin pieces such as metal turnings. If sodium or potassium ions are also in the solution, a precipitate of plutonium trifluoride may form.

Nitric acid solutions of plutonium are usually the preferred environment for plutonium. Nitric acid, however, even in concentrated form, will not dissolve plutonium metal satisfactorily. Dissolution may start but soon stops because of "passivation" of the plutonium metal surface. This effect can be eliminated by adding a trace of hydrofluoric acid. If the hydrofluoric acid is undesirable for further operations, it can be eliminated from the nitric acid solution by repeated fuming of the solution to near dryness and subsequent dissolution of the residue with nitric acid alone.

Because sulfuric acid attacks plutonium so slowly, it is not often used as a solvent. To prepare sulfuric acid solutions, it is simpler to prepare a hydrochloric acid solution of the metal, then convert it to a sulfuric acid solution by repeated evaporations to near dryness, and then take up the residues in sulfuric acid.

Plutonium Oxide Materials

Plutonium oxide samples are usually composed of PuO_2. The ease of dissolution of this material is related to the heat treatment the sample has received. Plutonium dioxide samples that have only been heated to 300ºC or 400ºC are soluble in hydrochloric acid with perhaps some heating. If the material has been heated to 800ºC to 900ºC, a pressurized dissolution method is required. This involves placing the sample in a heavy-walled borosilicate tube, adding concentrated hydrochloric acid with a trace of nitric and hydrofluoric acids, and heating the tube to about 160ºC. The tubes' contents are pressurized by inserting a rubber stopper in the open end of the tube and holding it in place with a clamp of a type that will allow the stopper to be released if the internal pressure becomes excessive. Samples on the order of several hundred milligrams can be successfully dissolved by this method in two to three hours.

A few plutonium dioxide samples may be encountered that have been heated to above 1100ºC or 1200ºC. The same releasable sealed tube method can be used for these, but the dissolution may take quite a bit longer. Careful temperature control is required for all kinds of samples to prevent release of the sealing stopper, which may result in an incomplete dissolution, or worse, release of some of the liquid contents of the tube.

Soluble Plutonium Compounds

Plutonium compounds that are known to be soluble should always be dissolved in a dilute (2 M) hydrochloric acid or nitric acid solution. It is important to avoid water or very dilute acid solutions because these can lead to unwanted changes in the plutonium species in solution if the sample solution is to be stored for more than several days. These effects are described in the chapter on hydrolysis and polymerization of plutonium in solution.

Stability of Plutonium Ions in Solution

The plutonium ions in solution that result from a dissolution procedure can nearly always undergo a process known as disproportionation. This process results in the eventual conversion of the original plutonium ionic species (III, IV, V, or VI) into a mixture of all four. There are steps that can be taken to minimize this effect or to return the ionic species to a single oxidation state. The important thing to realize is that a plutonium solution more than several weeks old may not retain its original proportion of ionic species. Disproportionation mechanisms are described in a later chapter.

CHAPTER 6

PLUTONIUM COMPOUNDS

Unlike most solid chemical compounds, plutonium compounds are not found in bottles on shelves or in the stock room. Any dry plutonium compound presents a health hazard because of the high probability that dispensing portions of it from a container in the open laboratory environment will create a dust, dangerous if inhaled. For this reason, most chemical manipulations with plutonium are conducted in solution in an analytical laboratory. When specific compounds are needed, they are prepared in a glove box or in a well ventilated area such as a fume hood in very small amounts in solutions whose effluents are filtered effectively.

Nevertheless, many plutonium compounds have been prepared in order to study their properties, as a general study of plutonium chemistry. Table 6-1 shows a list of simple binary compounds of plutonium to illustrate their most common properties and the fact that they exhibit a wide variety of colors, dependent on the oxidation state of the plutonium in the compound.

The two oxides Pu_2O_3 and PuO_2 are the most frequently encountered binary compounds of plutonium with oxygen. Plutonium dioxide is the compound formed when plutonium metal or many of its compounds are heated in air to several hundred degrees. Workers have found that the oxides prepared by heating different compounds of plutonium will have various colors ranging from yellow to nearly black. The green oxide is formed from the metal. All of the compounds in Table 6-1 will form this oxide when heated with free access to air. At temperatures below 800°C the ratio of oxygen atoms may not be exactly 2, but as they are heated to greater temperatures, the ratio becomes very close to 2. When PuO_2 is heated in a vacuum, the ratio may become

Table 6-1.

Some Common Binary Plutonium Compounds

Compound	Appearance	Density	Melting Point, °C
PuO_2	Green powder	11	2400
Pu_2O_3	Black, metallic	10	2250
PuO_3*	Green	4	($\rightarrow PuO_2$)
PuH_2	Gray flakes	decomp. 870	
PuN	Brown	14	burns
PuC	Silvery metallic	14	burns
PuF_3	Blue-green	9	1425
PuF_4	Pink - Tan		
PuF_6	Reddish Brown	51	
$PuCl_3$	Green	5	760
$PuBr_3$	Violet		
PuI_3	Violet		

* This formula refers to the peroxide, and not to a trioxide. See text below.

slightly less than 2. The effect of heating plutonium dioxide to high temperatures has received a great deal of study because of its importance to the stability of plutonium dioxide in nuclear reactor fuels.

An important property of plutonium dioxide to the analytical chemist is the difficulty encountered when it must be dissolved in various aqueous solvents. Material that has been heated to temperatures not greater than 300ºC will dissolve fairly easily in hydrochloric acid. That which has been heated to 800ºC or more requires a strong mixture of acids, heat, and pressure, which was described in Chapter 4 - The Dissolution of Plutonium Materials.

Plutonium sesquioxide, Pu_2O_3 is a black powder that can be prepared by the reduction of plutonium dioxide with carbon at elevated temperatures. It is slowly oxidized at room temperature by air, although it may remain stable for several weeks. Because it is unstable with respect to conversion to the dioxide, care must be exercised when manipulating it in the laboratory. It has been know to burn when being ground with a mortar and pestle in an air atmosphere.

Two other oxides of plutonium, PuO and PuO_3,—the monoxide and the trioxide—have never been successfully prepared. (The PuO_3 listed in Table 6.1 refers to the compound prepared by adding hydrogen peroxide to a solution of Pu (IV) in nitric acid, which is known as plutonium peroxide). Some workers have maintained that the first stages of the tarnishing of plutonium metal in air involve the formation of the monoxide, but if this is so, it probably is soon converted to the dioxide. With respect to the trioxide, a compound was isolated that was said to be the hydrated trioxide, $PuO_3.H_2O$, but others interpret the data as showing only the

existence of plutonyl hydroxide, $PuO_2(OH)_2$, a compound of hexavalent plutonium.

Plutonium peroxide, PuO_3, is a relatively unstable compound that is formed only by the slow and careful addition of hydrogen peroxide to a chilled nitric acid solution of Pu (IV). The solution turns brown at first, then red, and finally a green precipitate, which can be dried. It decomposes when heated. It has been useful as an intermediate in the removal of certain metal ions from impure plutonium solutions in process chemistry leading to plutonium metal production. This compound is not a true oxide in the sense that PuO_2 and Pu_2O_3 are. The O/Pu ratio is usually not exactly 3, and the precipitate usually contains occluded acid anions and water.

Plutonium hydride in bulk form is prepared by reaction of the metal and hydrogen at temperatures above 150ºC. The hydrogen-to-plutonium ratio is dependent upon the availability of hydrogen and is in the range of 2 to 3. The compound is thus not stoichiometric but usually falls in the range of $PuH_{2.2}$ to $PuH_{2.7}$. Hydride prepared under some conditions can be stable in air at room temperature for weeks, while other pre-parations may give a product that can be pyrophoric in air. Plutonium hydride has a black metallic appearance and behaves much like plutonium metal in its reactions with acid solutions. Thus, it is only very slowly reactive with nitric acid and reacts rapidly and vigorously hydrochloric acid solutions. Its chief importance is as an intermediate compound in the preparation of the nitride or in the preparation of plutonium metal in a powder form, which can be used in pluton-ium metallurgy. It is also a bothersome entity in the storage of plutonium metal in air since plutonium metal reacts with moisture in the

air to form a coating of plutonium hydride on the metal surface by the reaction

$$3Pu + 2H_2O \rightarrow 2PuH_2 + PuO_2. \qquad (6\text{-}1)$$
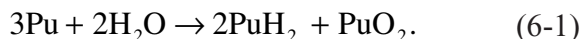
Plutonium nitride, PuN is a brown, stable compound that can be prepared by the reaction between plutonium hydride and nitrogen at about 230ºC. A second preparation method is the reaction between plutonium hydride and ammonia vapor at a higher temperature of 640ºC. PuN is the only known nitride of plutonium.

$$PuH_2 + N_2 \rightarrow PuN + 2H_2. \qquad (6\text{-}2)$$

$$2PuH_2 + 2NH_3 \rightarrow 2PuN + 5H_2. \qquad (6\text{-}3)$$
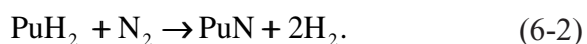
It has been important as a candidate material for plutonium fuels in power reactors utilizing mixtures of plutonium and uranium. Its density is 14, compared to 11 for plutonium dioxide, thus giving a higher power density in a reactor fuel element. It is volatile in a nitrogen atmosphere above 1000ºC, but does not melt until it reaches approximately 2580ºC. Its physical appearance is brown to black, hard and moderately brittle. Plutonium nitride decomposes to the oxide when heated to temperatures above 200ºC in air. It is unstable in moist air at room temperature, decomposing to plutonium dioxide. In hot water this reaction proceeds rapidly, leading to the formation of a black voluminous mass in the water. Plutonium nitride is most easily dissolved in nitric acid, as well as in hydrochloric, phosphoric, and sulfuric acids, although dissolution in sulfuric acid is slower than in the other three.

Plutonium carbide has been another important candidate for use in nuclear reactor fuels because of its high thermal conductivity and density. There are several different carbides, ranging from $PuC_{0.8}$ to PuC_2. They can be prepared at high temperatures by the reaction between graphite and plutonium metal, plutonium oxide, or plutonium hydride. (The sesquicarbide, Pu_2C_3, may be the only stoichiometric member of the carbides. This carbide and the monocarbide (which may not be exactly stoichiometric) are the most common carbides. Plutonium carbide usually has a metallic appearance, and the melting points of the most common ones are in the vicinity of 220ºC in an inert atmosphere. They are converted to the oxide when heated in air. If the temperature reaches 600ºC, the mono-carbide will ignite and burn. At room temperature, plutonium carbide is stable for several months in the massive form although the powdered form can be pyrophoric. Both the monocarbide and the sesquicarbide react with hot water to form plutonium (III) hydroxide plus hydrogen, acetylene, methane, ethane, and higher aliphatic hydrocarbons, an explosive gas mixture not unlike that formed by the reaction of water and calcium carbide.

Plutonium forms well characterized compounds with all of the four stable halogen elements. The tetrafluoride, PuF_4, however, is the only tetravalent plutonium halide. In the case of the chloride, bromide, and iodide, only the trivalent plutonium compounds have been isolated, although Pu (IV) does co-exist with these halide ions in solution. All of the halides are freely soluble in water except the fluorides, which are insoluble in the absence of large excesses of fluoride ion. The tetrafluoride is an important compound in the production of plutonium metal.

Plutonium hexafluoride, PuF_6, is a highly reactive compound formed by exposing plutonium tetrafluoride to fluorine at 700ºC in an inert atmosphere. Although it is a solid at room temperature, it is quite volatile, melts

at 51ºC, and boils at 62ºC. Its vapor pressure at its melting point is a little over 500 mm. The compound is moderately stable at room temperature, and its vapor resembles the reddish brown color of nitrogen tetroxide. It reacts violently with water by the reaction

$$PuF_6 + 2H_2O \rightarrow PuO_2F_2 + 4HF. \qquad (6\text{-}4)$$
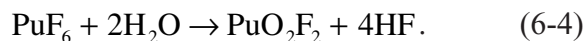
The compound is stable in sealed glass vessels provided there is no hydrogen fluoride or water present. Because of its volatility it is an extreme inhalation hazard. It has been used in studies of the separation of plutonium isotopes, but its reactivity with many other gases creates many difficulties in this application.

Other Plutonium Compounds

Hydroxides

Plutonium in the (III) and (IV) states forms two insoluble hydroxides. They are $Pu(OH)_3$, which is blue, and $Pu(OH)_4$, which is green. The trihydroxide is easily oxidized in air to $Pu(OH)_4$. Both are soluble in acids; however, they must be dissolved with an excess of acid to prevent polymer formation, which can be very troublesome for subsequent chemical operations (See the chapter on plutonium ions in solution.). When either of these compounds is formed from a plutonium solution, it will occlude many cations, so neither is a useful purification processes except to convert a plutonium solution from one anion system to another.

Oxalates

Plutonium (III) and (IV) also form oxalates, $Pu_2(C_2O_4)_3$ and $Pu(C_2O_4)_2$. These are both insoluble compounds, commonly formed by the addition of oxalic acid or an oxalate salt to the plutonium solution. They are useful in the purification of plutonium in the metal production process, in which case plutonium dioxalate is the compound that is used. These oxalates afford an effective separation of plutonium from americium, which is usually present as an impurity in aged plutonium materials. From the analytical chemistry point of view, oxalate solution samples or an oxalate sample derived from the supernatant liquid remaining after an oxalate precipitation should always be acidified to at least 2 $\underline{M}$ to avoid adsorption of plutonium on the walls of the sample container.

Sulfates

Two sulfates are also formed with the plutonium (III) and plutonium (IV) species $Pu_2(SO_4)_3$ and $Pu(SO_4)_2$. These violet or pink compounds are useful for the long-term storage of plutonium in a crystalline form in an inert atmosphere. The disulfate is ordinarily formed as plutonium disulfate dihydrate. This is the compound dispensed by the National Institute of Science and Technology as a plutonium isotopic ratio reference standard. Both compounds are soluble in water.

Iodates

The two iodates formed from plutonium (III) and (IV) are both insoluble compounds that are tan and pink, respectively, and are useful in certain research separation procedures. They are the only insoluble halate compounds of plutonium.

Phosphate

The plutonium (III) and (IV) phosphates are $PuPO_4$ and $Pu (HPO_4)_2$. The tetravalent phosphate compound is not the simple phosphate but the monohydrogen phosphate. This white compound also departs from the usual colorful hues of plutonium compounds while the plutonium (III) compound is purple. These two compounds are moderately soluble in water.

Carbonates

Single carbonates such as $Pu (CO_3)_2$ do not exist. Double carbonates can be prepared from $(NH_4)_2CO_3$ solutions, and Pu (VI) gives $(NH_4)_4PuO_2(CO_3)_2$, a bright green compound that is not too stable. K and Na carbonates also give double salts, which are useful in the study of the behavior of plutonium in natural environmental systems.

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CHAPTER 7

PLUTONIUM IONS IN SOLUTION

The solution chemistry of plutonium shows a complex interaction among the various oxidation states, complicated by conditions of acid strength, the presence of complexing anions, and in some cases by the effects of the alpha particle emission on the components of the solution. This chapter will discuss only aqueous solutions of plutonium, although a few non-aqueous environments will be mentioned.

Plutonium Oxidation States

The element shows five oxidation states in aqueous solution. These are summarized in Table 7-1.

Table 7-1.
Plutonium Oxidation State in Aqueous Solution

Oxidation In State	Ion	Color ($HClO_4$)
III	Pu^{+3}	Deep Blue
IV	Pu^{+4}	Brown
V	PuO_2^+	Colorless
VI	PuO_2^{+2}	Yellow to Pink
VII	PuO_5^{-2}	Dark Red

The heptavalent (VII) state is rare and prepared only under extreme oxidizing conditions. The other four oxidation states are common and can coexist together in simple acid solution where other reactions are not competing.

Plutonium (III) and plutonium (IV) are similar ions and are most commonly prepared by dissolution of the metal in hydrochloric acid. This yields the (III) state, which can be easily oxidized to the (IV) state by the addition of nitric acid. Plutonium (III) is slowly oxidized to the (IV) state by air, and is thus unstable with respect to the (IV) state over several days time under ordinary laboratory conditions. Over long periods of time, such as several days or longer, all four oxidation states will appear in a solution that was initially pure plutonium (III), so that it is difficult to predict the species present in a plutonium solution that has been standing for more than a few days. This transformation is known as disproportionation and will be discussed later.

The (V) and (VI) plutonium oxidation states are prepared by treating plutonium (IV) with a strong oxidizing agent such as potassium dichromate. Usually this treatment results in oxidation all the way to the (VI) state. Pure plutonium (V) solutions are generally prepared by careful treatment of a plutonium (VI) solution. The manipulation of the four oxidation states by chemical reagents is important in the separation of plutonium from impurities.

The color shown by plutonium solutions depends on both the oxidation state and the nature of the acid anion, which influences the degree of complexing of the plutonium species by the acid anion. Perchloric acid shows the least complexing action towards the four plutonium species. These complexes can bear either a positive charge or a negative charge, depending on the acid that is present.

Hydrolysis

Hydrolysis may occur with plutonium (III) and (IV) species in solutions of low acidity and the absence of complexing agents, and may possibly lead to unwanted reactions. A typical reaction is

$$Pu^{+4} + H_2O \rightarrow PuOH^{+3} + H^+. \qquad (7\text{-}1)$$
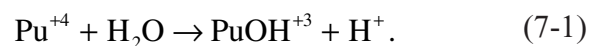
This can be followed by successive hydrolytic reactions until plutonium tetrahydroxide is formed:

$$PuOH^{+3} + H_2O \rightarrow Pu(OH)_2^{+2} + H^+ \qquad (7\text{-}2)$$

$$Pu(OH)_2^{+2} + H_2O \rightarrow Pu(OH)_3^+ + H^+ \qquad (7\text{-}3)$$

$$Pu(OH)_3^+ + H_2O \rightarrow Pu(OH)_4^+ + H^+. \qquad (7\text{-}4)$$
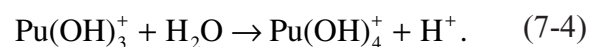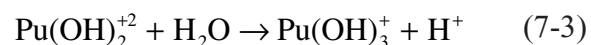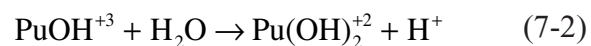
The tetrahydroxide is very insoluble with a calculated solubility product of about 10^{-56}. If the plutonium concentration is quite low, the plutonium tetrahydroxide might not form a visible precipitate but can adsorb onto container walls or minute particles in the solution, leading to unexpected decreases in the soluble plutonium concentration. If the initial plutonium species is Pu (III) and the trihydroxide is formed, it will be easily air oxidized to the tetrahydroxide. Hydrolysis is most likely to occur in solutions of Pu (IV). The relative ease of hydrolysis follows the order

$$Pu^{++++} > PuO_2^{++} > Pu^{+++} > PuO_2^+. \qquad (7\text{-}5)$$
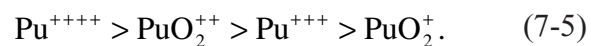
These hydrolysis reactions can be minimized or prevented by following the practice of always diluting a plutonium solution with acid of the same strength that is present in the solution, and never with water.

Polymerization

Another undesirable reaction that can take place in neutral or weakly acid solutions of plutonium (IV) is polymerization, which can convert plutonium to a form that is difficult to reverse or undo. The process is usually observed under conditions that are favorable only to partial hydrolysis, so that the insoluble plutonium (IV) hydroxide is not formed. It involves the linking of plutonium and oxygen (derived from hydroxyl ions) into long chains or more complex arrays of Pu-O units. The polymerization forms a soluble colloid, recognized by its bright green color if the plutonium concentration is greater than 1 g/L, which is about the lower limit that color is perceptible for small volumes of plutonium (IV) solutions (1 ml or less). The rate of formation of the colloid depends inversely on the acidity, and directly on the plutonium concentration and the temperature. A 1 g/l plutonium solution in 0.1 $\underline{M}$ nitric acid will easily form the colloid in less than an hour, and a 10 g/L solution in 0.3 $\underline{M}$ acid will behave similarly. An increase in temperature will hasten the polymerization. Plutonium in micromolar concentrations will polymerize at much slower rates at low acid concentrations.

The colloid is extremely stable and difficult to decompose. It can have equivalent molecular weights that range from the thousands to the billions. Plutonium in this colloidal state is very unreactive with other chemical reagents. It can be precipitated as a bright green solid by adding nitric acid, and the solid will redissolve with the addition of more nitric acid, reforming the soluble colloid. If a solution of the colloid is

evaporated to dryness and then reconstituted by the addition of water or dilute nitric acid, the plutonium is still in its polymerized or colloidal form. The polymeric form can only be destroyed effectively by heating it in fairly strong nitric acid with fluoride present, or with some other strong complexing agent.

Because of the ease with which this polymer is formed, it is essential to maintain stored plutonium solutions in an acid concentration of 2 <u>M</u> or greater at cool temperatures. Microconcentrations of plutonium are much less likely to form the polymer, but in these cases no visible color change may be detected if the polymer is formed because of the low plutonium concentration (0.01 g/L or less). The best protection against inadvertent use of poly-merized solutions is to work only with plutonium solutions that have been prepared from fresh dissolutions of plutonium metal.

Disproportionation

Another spontaneous reaction that affects the composition of a plutonium solution with respect to the presence of the ordinary four oxidation states, (III), (IV), (V), and (VI) is a reaction known as the disproportionation of the two species, plutonium (IV) and plutonium (V). This disproportionation reaction is not found in the chemistry of any other element in the periodic table.

The disproportionation reaction for Pu (IV) is

$$3Pu^{+4} + 2H_2O = 2Pu^{+3} + PuO_2^{+2} + 4H^+, \quad (7\text{-}6)$$
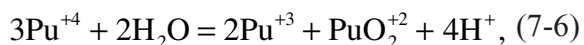
and the disproportionation reaction for Pu (V) is

$$3PuO_2^+ + 4H^+ = Pu^{3+} + PuO_2^{+2} + 2H_2O. \quad (7\text{-}7)$$
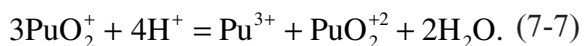
The reaction described by (7-6) is slower than that in (7-7) because it requires the formation of a Pu-O bond, while the reaction in (7-7) involves only an electron transfer. The equilibrium condition that is reached in disproportionation is

$$Pu^{+4} + PuO_2^+ = Pu^{+3} + PuO_2^{+2}. \quad (7\text{-}8)$$
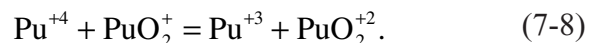
Disproportionation can occur in nearly any freshly prepared solution of plutonium. If initially the plutonium is all Pu (III), this is easily air-oxidized to furnish Pu (IV) which can disproportionate. The formation of Pu (VI) by disproportionation furnishes a source of Pu (V) because the Pu (VI) is easily reduced by hydroxyl ions formed by the effects of alpha particle radiation on the solvent water.

The equilibrium concentrations of equation (7-8) are strongly affected by the acid concentration. Repression of dispro-portionation can be achieved by storing plutonium solutions in 2 <u>M</u> acid or greater. The presence of complexing agents for Pu (IV) will also repress disproportionation. In any case, an aged plutonium stock solution, even in strong acid, should not be assumed to contain only one of the four plutonium species, (III), (IV), (V), and (VI).

Radiolysis

In aqueous solutions the alpha particle emission of the plutonium can break a bond in the water molecule, thus producing OH radicals, which can react with Pu in the (VI), (V), or (IV) oxidation states to reduce them all the way to the (III) state, depending upon the total amount of energy absorbed over a period of time by the solvent from the alpha particle emission.

This effect is significant only for solutions containing concentrations greater than several hundred milligrams of plutonium per liter. In a dilute nitric acid solution containing 1 gram per liter of plutonium, enough energy is absorbed by a liter of the solution in 29 hours to reduce all of the Pu, if in the (VI) state, to Pu (V). The same solution will absorb enough energy from the alpha particles in 6 days to reduce all of the plutonium to Pu (III). This assumes that there is no air oxidation of the Pu (III), or that other competing reactions such as disproportionation are not occurring. Once again, it is unsafe to assume that the original proportion of ionic concentration in a stored plutonium solution will remain the same over a period of time.

CHAPTER 8

COMPLEXES OF PLUTONIUM

Complex formation occurs with all four species of plutonium in aqueous systems. There are hundreds of inorganic and organic complexes. This chapter will discuss only a few of the most common and useful complexes for analytical chemistry procedures. The use of complexing agents for plutonium is important because they can be employed to minimize the effects of hydrolysis and disproportionation. Plutonium complexes can reduce significantly the amount of available plutonium that can participate in hydrolysis and disproportionation so that these effects do not interfere with other desirable reactions.

Inorganic Complexes

The stability of an inorganic complex with plutonium depends on the plutonium species that reacts with the complexing agent. In general, plutonium (IV) forms the most stable complexes because it has the highest ionic charge compared to its ionic size. The order of complex stability for all four of the common oxidation states of plutonium is

$$Pu^{4+} > Pu^{3+} > PuO_2^{2+} > PuO_2^{+}$$
or
$$Pu\ (IV) > Pu\ (III) > Pu\ (VI) > Pu\ (V).$$
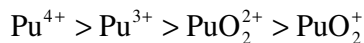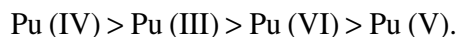
Notice that the stability of the plutonium complexes decreases with decreasing charge on the cation. This follows a general rule for complex stability in relation to the ionic charge. This stability order is not unexpected, at least with regard to Pu (IV)

forming the most stable complexes, since other elements that exhibit +4 oxidation states also show enhanced complex stability, such as Zr (IV) and Th (IV).

Complexes with Monovalent Anions

The four most common monovalent anions that are encountered show the following order of complex stability, especially for complexes with Pu (IV):

$$F \rightarrow NO_{3-} \rightarrow Cl \rightarrow ClO_{4-}.$$
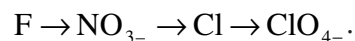
This order is reversed with respect to chloride and nitrate for Pu (III).

As mentioned in an earlier chapter, perchloric acid, $HClO_4$, is not considered a complexing agent for any plutonium species. It is listed in the sequence above because dilute perchloric acid solutions are important in the study of plutonium chemistry to provide a medium where complexing does not occur to a significant extent. The other three anions, however, form complexes with plutonium. Although not listed, bromide and iodide ions form plutonium complexes, although to a lesser extent than does a chloride ion.

Pu (III) Complexes with Monovalent Anions

The fluoride complex is the most stable, and will form a precipitate in the presence of excess fluoride ion. Thus, PuF_3 is easily oxidized to PuF_4 in solutions with an excess of fluoride and that are exposed to the air. Both the Pu (III) and Pu (IV) fluoride compounds are important in aqueous separation processes for the purification of plutonium.

Nitrate complexes of Pu (III) do not exist because they are unstable with respect to oxidation by nitrate ion to Pu (IV) complexes.

In hydrochloric acid or chloride solutions two complexes are known, $PuCl^{++}$ and $PuCl_2^+$, both of which are formed as the chloride concentration increases from 1 $\underline{M}$ to 8 $\underline{M}$. These are not strong complexes.

In thiocyanate solutions two Pu (III) complexes have been characterized, $Pu(SCN)^{2+}$ and $Pu(SCN)_2^+$; these have stability constants a little greater than one. Negatively charged thiocyanate complexes of Pu (III) are also known to exist, based on data with anion exchange resins, but stability constants are not available. Thiocyanate complexes are important in the separation of the lanthanide group of elements from the actinide group, which contains plutonium. Thiocyanate forms stable complexes with all of the elements that have an oxidation state of +3 in these two groups. Because the stability constants for the thiocyanate complexes of the lanthanide elements are less than those of the actinide elements, the thiocyanate complexes can be used to achieve separation of the two groups of elements. The need for such group separations is usually encountered only in mixtures of plutonium and fission products.

Pu (IV) Complexes with Monovalent Anions

Fluoride complexes result from the addition of fluoride to form a series of positively charged fluoride complexes including PuF^{3+}, $(PuF^{22}$, and PuF_3^+, until the neutral PuF_4 is formed, which precipitates in dilute nitric acid as additional fluoride is

added. The tetrafluoride may be somewhat slow to precipitate unless other cations such as potassium are present. This fluoride is also somewhat soluble at high acid concentrations or in the absence of excess fluoride. Under these conditions, it can exist in equilibrium with the positively charged complexes. An excess of fluoride is necessary, therefore, to precipitate all of the plutonium as the tetrafluoride. Plutonium tetrafluoride is an important compound in the purification of plutonium and in some methods for metal production.

Both positive and negative chloride complexes of Pu (IV) are known. The first complex, $PuCl^{3+}$, can be formed in as low as 0.3 $\underline{M}$ hydrochloric acid. With increasing chloride concentration, all chloride complexes are formed up through $PuCl_6^{2-}$, which amounts to 75% of the chloride complexes in 12 $\underline{M}$ hydrochloric acid, but only 5% in 8 $\underline{M}$ hydrochloric acid. This enables the selection of several different chloride complexes by varying the chloride concentration.

Bromide complexes of Pu (IV) form in similar fashion to the chloride complexes, but they are somewhat weaker. Unlike the chloride complexes of Pu (IV), there are no definite indications of the existence of negatively charged bromide complexes.

The most important nitrate complex, from an analytical separation point of view, is the hexanitrato complex, $Pu(NO_3)_6^{-2}$, which is formed in 7 $\underline{M}$ nitric acid or stronger. This complex is useful in both solvent extraction processes and ion exchange processes. It is interesting that this complex changes the brown color of uncomplexed Pu (IV) to green.

Pu (V) Complexes with Monovalent Anions

Aqueous solutions that contain only PuO_2^- and no other plutonium species are colorless, which correlates with the fact that complexing by inorganic ligands is weak, if it occurs at all. No fluoride complex is known. There is some evidence that a weak complex with nitrate may be formed with high nitrate concentrations. A chloride complex has been identified—PuO_2Cl, but it is a weak complex.

Pu (VI) Complexes with Monovalent Anions

No fluoride complex is known, and aqueous solutions of PuO_2^{++} show little tendency to form complexes with a nitrate ion, a surprising circumstance in view of the stable complexes formed between UO_2^{++} and nitrate ions.

It is also surprising that the chloride anion forms a series of complexes with plutonyl ions, thus reversing the order of stability for nitrate and chloride that exist for the other plutonium oxidation states. As the chloride concentration is increased from 1 $\underline{M}$ to 8 $\underline{M}$, a succession of complexes is formed: PuO_2Cl^+, PuO_2Cl_2 and $PuOCl_4$. The tetrachloro complex can be useful in ion exchange separations.

Complexes with Divalent Anions

In general, complex formation with divalent anions leads to stronger complexes than with monovalent anions. Among the more common divalent inorganic anions, such as carbonate, sulfamate, oxalate and sulfate, the order of stability for complexing with plutonium (IV) is

$$CO_3^{-2} > SO_3^{-2} > C_2O_4^{-2} > SO_4^{-2}.$$
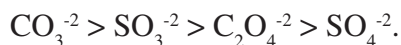
Thus, carbonate forms the strongest complexes, and sulfate forms the weakest complexes, although in this case the sulfate complexes are significant.

Pu (III) Complexes with Divalent Anions

The carbonate and sulfite complexes with Pu (III) are relatively unstable because of their ease of oxidation to Pu (IV) in aqueous solutions exposed to the air.

Oxalate complexes of Pu (III) are known to exist, and their study was important in the early history of plutonium chemistry because of the use of oxalate in the purification of plutonium, even though it turned out that the Pu (IV) formed the most important oxalate complexes. In solutions not exposed to the air, oxalate complex formation begins at about a pH of 1; at lower pH values Pu (III) shows complex formation as $Pu(HC_2O_4)^+$. As the pH is increased, higher complexes with pure oxalate ion are formed until $Pu(C_2O_4)_4^{5-}$ is reached at a pH value of 3.5; at a pH of 6, this complex is the predominant species. Each of the complexes in this series has a stability constant of greater than 10^8. It is important to be aware that the plutonium in these complexes is rapidly oxidized to Pu (IV) once air is admitted to the solution environment.

Sulfamic acid, HSO_3NH_2, in 2 $\underline{M}$ solution forms the complex $Pu(SO_3NH_2)^{3+}$, in which approximately half of the plutonium is complexed. This is not considered a strong complex.

Pu (IV) Complexes with Divalent and Trivalent Anions

As is the case for monovalent anion complexes with Pu (IV), some of the most important divalent anion complexes are formed with Pu (IV). Experienced plutonium chemists often remark that Pu (IV) solution chemistry is a chemistry of complexes, not of uncomplexed plutonium.

The sulfate complexes have been thoroughly investigated since the discovery of plutonium in the early 1940s. Plutonium (IV) sulfate complexes are formed in even low concentrations of sulfate ion or sulfuric acid. The complex, $Pu(SO_4)^{2+}$ exists in potassium sulfate concentrations as low as 0.03 $\underline{M}$, in a nitric acid medium of 1.5 $\underline{M}$. With the addition of more sulfate, the neutral species $Pu(SO_4)_2$ is formed at about 0.15 $\underline{M}$ sulfate. In this same medium, the highest complex is probably $Pu(SO_4)_4^{4-}$, which becomes predominant at 0.65 $\underline{M}$ sulfate concentration. These observations demonstrate the ease with which Pu (IV) forms stable complexes with the $SO_4^=$ anion. Carbonate and sulfite complexes with Pu (IV) have not been characterized.

The phosphate ion is the only trivalent inorganic anion studied as a complexing ligand for Pu (IV). The first complex, $Pu(HPO_4)^{2+}$, is formed at about 0.03 $\underline{M}$ H_3PO_4. The uncharged species, $Pu(HPO_3)_2$, was found to predominate at 0.1 $\underline{M}$ phosphoric acid, and increasing the acid concentration to greater than 3 $\underline{M}$ gave the complex, $Pu(HPO_3)_6^{6-}$. All of the phosphate complexes show stability constants of in the range of 10^8 to 10^{12}. These complexes are important in separations of small amounts of plutonium from large amounts of uranium and fission products in the processing of reactor-produced plutonium. The bismuth phosphate process for separating plutonium from the Hanford Reactors' uranium fuel rods was the first process used for the separation of plutonium from uranium and fission products. This process has since been replaced by more economical methods.

Pu (V) Complexes with Divalent Anions

As described earlier, PuO_2^+ is expected to form the weakest complexes of the four plutonium ions in aqueous solution because of its low charge and relatively large ionic size.

Oxalate anions, however, form several complexes with PuO_2^+ in weakly acid solutions near a pH of 4. The three complexes, $PuO_2(HC_2O_4)$, $Pu(C_2O_4)^-$, and $Pu(C_2O_4)_2^{3-}$, have stability constants of 200, 7000, and 10^6, respectively. Aside from these, no other divalent inorganic anions are known to form Pu (V) complexes.

Pu (VI) Complexes with Divalent Anions

Because PuO_2^{2+} has twice the ionic charge but the same ionic size as PuO_2^+, it can form more stable complexes. Some of these complexes are valuable in separation chemistry and analysis. The plutonyl cation, PuO_2^{2+}, is the plutonium analogue of the uranyl cation, UO_2^{2+}. An important difference between the two is that the uranyl cation is the most stable of the common uranium cations, while plutonyl cation is unstable with respect to reduction to Pu^{4+}, making studies of some complexes of Pu (VI) difficult.

Carbonate complexes with Pu (VI) solutions have been studied in strong potassium carbonate solutions, and complexes with very large stability constants have been observed in these solutions. The addition of dilute Pu (VI) to 45% potassium carbonate gives an intense green color to the mixture. It is thought that the complex responsible for this color is $PuO_2(CO_3)_3{}^{4-}$. Strong ammonium carbonate solutions increase the solubility of Pu (VI) hydroxide, $PuO_2(OH)_2$, which is formed by the addition of potassium hydroxide solution to Pu (VI) solutions. Adding ammonium carbonate solution to a Pu (VI) solution in dilute nitric acid results in an intense green precipitate with the composition $(NH_4)_4PuO_2(CO_3)_3$. When more dilute solutions of ammonium carbonate, between 1% and 5%, are added, an intense red color results, and the complex that is formed is thought to be $(NH_4)PuO_2(CO_3)^+$. With stronger ammonium carbonate solutions, a complex with the composition $(NH_4)PuO_2(CO_3)_2{}^-$ is probably formed. The stability constants of the carbonate complexes are very high, 10^{13} or greater. Carbonate complexes of Pu (VI) are considered to be important in the studies of the transport of plutonium in environmental systems. There is strong evidence that when extremely dilute concentrations of plutonium exist in natural water systems, as the result of fallout from mid-twentieth century nuclear weapon tests in the atmosphere, the predominant plutonium species may be Pu (V) and Pu (VI).

Sulfate forms stable complexes with Pu (VI) in sulfuric acid concentrations of 0.1 to 4 $\underline{M}$. The complexes are probably neutral, $PuO_2(SO_4)$ in the lowest concentrations and anionic in the higher acid concentrations, where two complexes may exist— $PuO_2(SO_4)_2{}^{2-}$ and $PuO_2(SO_4)_3{}^{4-}$. Results of studies of these complexes suggest that greater than 90% of the plutonium is complexed. When ammonium sulfate is used instead of sulfuric acid, the proportion of complexed plutonium is even higher, probably because of a larger availability of sulfate ions in salt solutions than in acid solutions, where some of the acid anions exist as $HSO_4{}^-$.

Oxalate complexes of Pu (VI) are complicated by the tendency of oxalate ions to act as a reducing agent for Pu (VI). Nevertheless, there is reliable evidence that the oxalate anion, $C_2O_4{}^{2-}$, forms two complexes. In 1 $\underline{M}$ nitric acid solutions, with a range of 0 to 4 $\underline{M}$ ammonium oxalate, a neutral complex, $PuO_2(C_2O_4)$, and an anionic complex, $PuO_2(C_2O_4)_2{}^{-2}$ are formed. The anionic complex, of course, is found at the higher oxalate concentrations. Both complexes have high stability constants of 10^6 and 10^{11}, respectively.

The monovalent phosphate ion, H_2PO_4 also forms complexes with Pu (VI), even in low concentrations of phosphoric acid. In 0.02 $\underline{M}$ phosphoric acid, a cationic Pu (VI) complex, $PuO_2(H_2PO_4)^+$, is formed with a high stability constant of 8000. When the phosphoric acid concentration is increased beyond 0.2 $\underline{M}$, the neutral complex $PuO_2(H_2PO_4)_2$ is formed. It can be precipitated with the addition of methanol to the phosphoric acid solution.

Organic Complexes

Some of the plutonium ionic species form very stable complexes with organic ligands, some of which are soluble in water, and others in organic solvents. These organic ligands have been sought after and evaluated since the mid-1940s when sufficient plutonium (milligram amounts) became available. By 1947, over 500 possible ligands had been identified and studied for their applicability in the separation of plutonium from other elements. The few that have played an important part in separation processes for metal production or for analytical chemistry purposes are the subject of this discussion. Their descriptions will follow without regard to plutonium oxidation states.

Acetate Complexes

In Pu (III) solutions that are protected from oxidation, two complexes are formed, $Pu(C_2H_3O_2)^{2+}$ and $Pu(C_2H_3O_2)_2{}^+$, with stability constants of 200 and 2200, respectively. Plutonium (IV) forms a series of highly stable acetate complexes at pH values less than 4.5. The addition of acetate to the plutonium solution changes the color from brown (or green) to purple-orange. Five complexes have been identified containing between one and five acetate ligands. Their stability constants range between 10^9 and 10^{23}. Plutonium (VI) can be precipitated from sodium acetate solutions as $NaPuO(C_2H_3O_2)$. Studies on the supernatant solution above the precipitate indicate the presence of the complexes $PuO(C_2H_3O_2)^+$, $PuO(C_2H_3O_2)_2$, and $PuO(C_2H_3)_3{}^-$ with stability constants of 10^3, 10^6, and 10^7 respectively.

Ethylene Diamine Tetracetic Acid Complexes (EDTA)

All four plutonium species form complexes with EDTA, and they are among some of the most stable complexes found in aqueous systems. The structure of the ligand is

$HOOCCH_2$ CH_2OOH

$N\text{-------}CH_2\text{----}CH_2\text{---------}N$

$HOOCCH_2$ CH_2OOH .
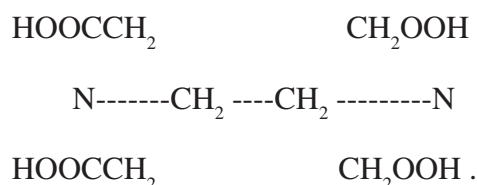
It is common for the sodium salt of EDTA to be used instead of the acid. In this discussion, $EDTA^{4-}$ refers to the ethylene diamine tetra acetic acid molecule in which the four carboxyl hydrogen atoms have been removed, leaving the radical with a charge of 4-.

The complex formed with Pu (III) is $Pu(EDTA)^+$,

$$Pu^{3+} + EDTA^{2-} \rightarrow Pu(EDTA)^+, \qquad (8\text{-}1)$$

where the Pu atom replaces the hydrogen atoms on two adjacent acetic acid groups whenever the Pu/EDTA ratio is less than one. The stability constant (10^{18}) of this complex is so high that at a pH value of 11 plutonium (III) trihydroxide cannot be precipitated. If the Pu/EDTA ratio is increased to 2, a second complex is formed:

$$2Pu^{+3} + EDTA^{4-} \rightarrow Pu_2(EDTA)^{2+}, \qquad (8\text{-}2)$$

where the second Pu atom chelates with the two remaining acetic acid groups, forming $Pu_2(EDTA)^-$, and its stability constant is also about 10^{18}. If the Pu/EDTA ratio exceeds 2, then some of the plutonium atoms will not be complexed.

Plutonium (IV) forms even stronger complexes with EDTA than does Pu (III). In

1 $\underline{M}$ nitric acid, the stability constant for Pu(EDTA)$^{2-}$ is about 10^{24}:

$$Pu^{4+} + EDTA^{2-} \rightarrow Pu(EDTA)^{2+}. \qquad (8\text{-}3)$$
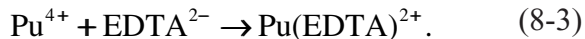
For a Pu/EDTA ration of 2, the complex formed with both EDTA chelating sites is

$$2Pu^{4+} + EDTA^{4-} \rightarrow Pu_2(EDTA)^{4+}, \qquad (8\text{-}4)$$
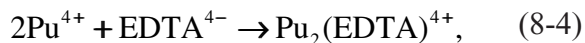
whose stability constant is about 10^{27}. While the Pu (IV) specie forms very stable complexes with EDTA, it is known that many other metal cations do also. In general these chelated complexes are not very useful for separating plutonium from other metals.

Plutonium (V) is chelated by EDTA only at pH values >4. The complex is formed by the reaction

$$PuO_2^+ + EDTA^{2-} \rightarrow PuO_2(EDTA)^- \qquad (8\text{-}5)$$
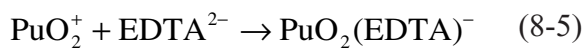
with a stability constant of about 10^{10}. This is the weakest of the plutonium complexes with EDTA.

Plutonium (VI) is complexed by EDTA according to the reaction

$$PuO_2^{2+} + EDTA^{2-} \rightarrow PuO_2(EDTA) \qquad (8\text{-}6)$$

with a stability constant of about 10^{16}. This blue, chelated complex is unstable and over a period of days, at pH values of 3 to 5, is reduced to form the Pu (IV) EDTA complex. In the presence of excess EDTA, the Pu (VI) complex will be reduced to the Pu (V) species. The complex with a ratio of Pu/EDTA = 2 is not formed.

Citric Acid (2-Hydroxy Tricarboxylic Acid) Complexes

Citrate complexes are formed only with Pu (IV), and one of these is exceptionally stable. Citric acid, $C_6H_8O_7$, is a common organic acid with three carbonyl groups, each of which can lose a hydrogen atom in aqueous solutions to form the citrate anion, $C_6H_5O_7^{3-}$. At citrate concentrations as low as 10^{-15} $\underline{M}$ the citrate complex, Pu $(C_6H_5O_7)^+$ has been detected.

At citrate concentrations between 10^{-13} and 10^{-15} $\underline{M}$ the complex, $Pu(C_6H_5O_7)_2^-$ is formed. At citrate concentrations >10^{-13} there is evidence for a higher complex, but it has not been characterized. The stability constants for the mono- and dicitrato forms are 10^{15} and 10^{29}, respectively.

Lactic Acid (α-Hydroxy Propanoic Acid) Complexes

Lactate acid forms a complex with Pu (III) and Pu (IV), but not to a significant degree with the other plutonium oxidation states. At lactate concentrations >10^{-4} $\underline{M}$ only one complex is formed, the neutral $Pu(C_3H_5O_3)_4$. The positively charged mono-, di-, and trilactato complexes are probably formed at higher lactate concentrations because plutonium can be separated from other actinides by cation exchange resins when the eluting reagent is 0.4 $\underline{M}$ αμμονιυμ λαχτατε.

α-Hydroxy Isobutyric Acid Complexes

Like lactic acid, ammonium salts of α-hydroxy isobutyric acid form cationic complexes with Pu (II) and Pu (IV), where the tetravalent specie forms complexes with the higher stability constants. The actual values of the stability constants are unavailable.

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CHAPTER 9

LABORATORY PURIFICATION METHODS

Some analytical procedures for plutonium or for impurities in plutonium require that the sample impurities be removed before proceeding with the plutonium analysis, or that the plutonium be removed from the sample in order to allow accurate determinations of the impurities. This chapter discusses the chemical principles underlying some of these purification methods.

The organic ligands that are useful for plutonium separations come in several forms. Typical of the solid forms, insoluble in aqueous systems, are the very important ion exchange resins. Other types are those soluble in organic solvents but insoluble in aqueous systems. Two examples of these are tributyl phosphate (TBP) and thenoyl-trifluoroacetone (TTA). Yet another type is found in organic acids or their sodium salts, and is soluble in aqueous systems. This type is represented by the ethylene diamine tetra acetic acid (EDTA) family.

Liquid-Liquid or Solvent Extraction

Since the first gram quantities of plutonium became available in 1944, a large amount of work has been directed toward identifying organic ligands that would form complexes with plutonium. It was hoped that some of these ligands might facilitate its separation from reactor fuels, and its recovery from waste residues. As early as 1947 more than 500 organic compounds had been evaluated, and currently there have been thousands tested.

Ether and Ketone Extractions

Two of the earliest organic systems diethyl ether and methyl isobutyl ketone, which are now only of historical interest, did not use organic ligands as such but employed organic solvents for the separation of the inorganic complex $Pu(NO_3)_6^{2-}$, described earlier. This complex, in the presence of large amounts of aluminum nitrate, is extracted with high efficiency from impure plutonium solutions into diethyl ether or methyl isobutyl ketone. These procedures, however, were quickly replaced by others that did not involve the use of such flammable solvents.

Organic Complexing Agents Soluble in Organic Solvents

This is the class of ligands that are ordinarily dissolved in an organic solvent and used to extract the particular plutonium species from an aqueous system by forming a plutonium complex that is preferentially soluble in the organic phase but not in the aqueous phase. Typical organic extractants of this class are tributyl phosphate in kerosene, thenoyl trifluoroacetone in benzene or xylene, and quaternary alkyl amines in chloroform. There are many others that have been used for specialized purposes, but this description will be confined to these three, which are among the most commonly used.

Tributyl Phosphate

This complexing agent is important in both industrial and analytical laboratory applications. It is used to react with the plutonium (IV) hexanitrato complex, $Pu(NO_3)_6^{2-}$ described earlier. For effective extraction of the plutonium into the kerosene

phase, a high nitrate concentration must be present in the aqueous phases. This is achieved by using 8 M nitric acid or saturated aluminum nitrate. The plutonium is first extracted into the organic phase, leaving behind the impurity elements in the aqueous phase. The plutonium can then be removed or stripped from the organic phase with a 1 M nitric acid solution containing a reducing agent such as hydroxylamine. This reduces the extracted Pu (IV) species to Pu (III), which is not soluble in the organic phase and returns to the aqueous phase. Purity of the tributyl phosphate reagent is important because the presence of mono- or dibutyl phosphate will hinder severely the stripping of the plutonium from the kerosene phase. These impurities can be removed by washing the kerosene solution with dilute sodium hydroxide solution before use of the tributyl phosphate solution. A commonly used concentration of the tributyl phosphate is 30% in the kerosene phase.

When the plutonium (IV) is in nitric acid, the optimum extraction into the organic phase occurs at 7 M HNO$_3$, and the extraction coefficient is 35 to 50. If most of the nitrate is furnished by aluminum nitrate instead of nitric acid, the extraction coefficient rises dramatically to over 30,000. In this case, the optimum conditions are 1 M nitric acid and 2.7 M aluminum nitrate. The reason for this is that nitric acid is also extracted by tributyl phosphate, but aluminum nitrate is not. Thus, a favorable nitrate concentration for plutonium extraction can be maintained with an excess of aluminum nitrate over nitric acid; if nitric acid alone is present, its concentration is depleted.

The extracted Pu (IV) species is Pu(NO$_3$)$_4$. This is a true coordination complex, with the central Pu atom exhibiting a coordination number of 6. Pu (III) is extracted also, but only to a minor extent so it is important that the plutonium in the solution to be extracted is stabilized as Pu (IV). Since uranyl nitrate is also extracted efficiently, this is not a good separation procedure for plutonium from uranium.

Thenoyl Trifluoro Acetone (TTA)

This chelating agent forms very stable complexes with Pu (IV) that are insoluble i-

water but soluble in aromatic organic solvents such as xylene. The reaction for the chelate formation is

$$Pu^{4+} + 4HTTA \rightarrow Pu(TTA)_4 + 4H^+. \quad (9\text{-}1)$$
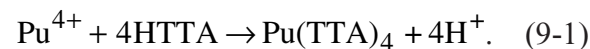
TTA is a member of the class of compounds know as beta diketones. These can exist in the enol form, where the position of a hydrogen atom attached to a carbon atom can form a bridge between the two ketone oxygen atoms. This form has an enhanced solubility in water so that it can react with the aqueous plutonium atom, with the subsequent transfer of the chelated plutonium atom into the solvent that contains the TTA. The reaction above generates hydrogen ions so that increasing the aqueous acid concentration will tend to repress the reaction. The stability of the Pu (IV) complex is so great, however, that even in 4 M acid solutions, the plutonium extracts into the organic solvent with close to 100% efficiency. This gives a good separation from thorium, which also forms a TTA chelate, but one that extracts only from aqueous solutions with an acid strength of less than 0.1 M. Zirconium and iron extract with the plutonium, but none of the lanthanides or

actinides in the +3 oxidation state is extracted at 1 $\underline{M}$ acid concentrations.

This extraction procedure is the basis for an excellent method of preparing "weightless" films of americium-free plutonium for alpha particle spectrometry.

Extraction with Quaternary Amines

Many long-chained alkyl amines, when dissolved in an organic solvent such as xylene, kerosene or chloroform, will extract plutonium ions or complexes from aqueous solutions. Particularly useful are the quaternary ammonium cations with the basic formula $R_aR_bR_cR_dN^+$, usually combined with nitrate ions to form a quaternary ammonium salt. The Rs denote various alkyl groups, which are, in the case of the extracting compounds, long-chain residues from organic acids. Although the general formula above denotes four organic residues, they are not necessarily all different, and quite often three are identical while the fourth is quite often the methyl residue, CH_3^+.

In general, the conditions that favor high extraction coefficients for Pu (IV) are high nitrate concentration, medium acid concentration in the aqueous phase, and high molecular weights for three of the organic residues attached to the nitrogen atom of the quaternary ammonium nitrate. The high nitrate concentration can be achieved with 5 to 7 $\underline{M}$ ammonium nitrate, and the medium acid concentration is usually placed at 3 $\underline{M}$ nitric acid concentration. Some compounds will also extract hydrogen ion from the aqueous phase. This depletes extractant otherwise available for plutonium extraction. In these cases, the nitric acid concentration can be reduced, as long as the

total nitrate is maintained at 5 to 7 $\underline{M}$ with ammonium nitrate. The concentration of the quaternary ammonium nitrate is usually 0.1 to 0.5 $\underline{M}$ in the organic solvent. When tridecylmethylammonium nitrate is used, three of the organic residues are 10-carbon chains, while the methyl group contains only one carbon. This reagent yields extraction coefficients near 5000 for Pu (IV). Increasing the three organic residues to 12-carbon chains, as in trilaurylmethylamonium nitrate, shows extraction coefficients of around 13,000. This method of extraction can be quite successful in the separation of plutonium from large amounts of uranium, since extraction coefficients for U (VI) are small. The plutonium extracts as a negatively charged nitrate complex, probably $Pu(NO_3)_6^{-2}$. This method of extracting plutonium is closely analogous to the use of anionic ion exchange resins, to be discussed later.

The plutonium in the organic phase can be back-extracted into dilute nitric acid (0.1 $\underline{M}$). Once the plutonium is in this dilute acid solution, enough concentrated nitric acid should be added to make a solution at least 2 $\underline{M}$ in order to prevent hydrolysis and polymerization of the plutonium.

Ion Exchange Resins

Ion exchange resins are made by attaching organic complexing groups, sometimes called active sites, to a stable and insoluble substance such as polystyrene. At the time of manufacture the polystyrene is cross-linked with 1% to 12% of divinylbenzene polymer, which controls the water permeability of the resin; the higher the cross-linkage, the less permeable is the resin. The resin is dispersed during manufacture into various sizes of

beads, which can range from several millimeters in diameter to fractions of a millimeter. The active groups are of two types, (1) those which will form a complex with cations, and thus are known as cation exchange resins, and (2) those which will form a complex with anions and are known as anion exchange resins. In the commonly used ion exchange resins, such as the Dowex or Amberlite resins, sulfonate groups ($-SO_3^-$) form the active sites in the polymer for cation exchange, and trimethyl ammonium groups ($-CH_3)_3N^+$) are the active sites for anion exchange resins. The permeability of the resin bead controls the diffusion rates of the ions from the solution into the bead. This affects the overall rate of reaction between the active site on the resin and the ion it absorbs. The size of the bead is important because it affects the time required for a given amount of an ion to be absorbed within the bead. Large bead sizes have slower absorption times.

The two major techniques used in ion exchange procedures are known as batch operations and column operations. In a batch operation the ion exchange resin is mixed in a beaker with the solution of the ions to be absorbed and stirred until equilibrium is reached between the resin and the solution. This technique is useful in measuring the distribution coefficient between the solution and the resin. In column operations, a slurry of the resin mixed with distilled water is poured into a vertical plastic or glass column, which is loosely plugged with glass wool at its narrowed bottom to retain the resin until the column is filled with the slurry. It is important to avoid air spaces in the column. The water will drain from the column until it reaches the top of the resin bed. The top of the column should be attached to a wider-diameter reservoir to enable the

addition of solutions. In the analytical laboratory, column diameters are usually less than 1 cm, with a length-to-width ratio of 10. Glass is preferred over plastic for developing procedures because it gives clear visibility of the color and size changes that may occur in the resin bed as different reagents pass through it. When working with a milligram or more of plutonium, it is quite easy to see the color of the plutonium adsorbed at the top of the column.

There are several precautions to observe for successful plutonium separations by ion exchange procedures. Whether the plutonium is to be absorbed or the impurities are to be absorbed, it is important to use uniformly sized resin beads. This ensures that the reaction between each bead and the solution is proceeding at a nearly uniform rate for all the beads. Commercially supplied resins are packaged with a specific size designations, but in fact any one package may contain a range of sizes. By dispersing the resin in water in a large graduated cylinder, it is possible to eliminate coarse and very fine beads by selecting the beads, which settle in a specific time. The uniformity of the size of the beads is more important than their actual size. In many cases, carrying out this sizing procedure from a package that is labeled as containing 100–200 mesh beads is adequate for many plutonium separation procedures. Sometimes it will be necessary to start from a package that contains 200–400 mesh resin. This may be the case for separating plutonium from other actinides with cation resins. A second precaution is the proper pre-equilibration of the resin before the preliminary separation procedure. The beads are ordinarily loaded into a plastic or glass column as an aqueous slurry. After the column is filled with resin, the resin should

be washed with the same type and concentra-tion of aqueous solution that contains the plutonium material to be placed on the resin column. That is, if the plutonium is contained in 7 $\underline{M}$ nitric acid, the resin column should first be washed thoroughly with 7 $\underline{M}$ nitric acid.

Cation Exchange Resins

Cation Exchange Resins are usually supplied in the hydrogen form, which means that the active site at the sulfonate residue is occupied by a hydrogen ion, which can then be replaced by another cation when used for separation procedures.

Other forms can be prepared from the hydrogen form, such as the sodium form that is prepared by soaking the resin in a sodium chloride solution, then washing it with water until a negative chloride test is obtained. The hydrogen form, however, is the one most commonly used.

All three of the most common plutonium species, Pu (III), Pu (IV), and Pu (VI) are absorbed readily from dilute (< 2 $\underline{M}$) acid solutions by cation exchange resins such as Dowex 50 or Amberlite IT 120. The absorption of the cation into the resin is described quantitatively by the distribution coefficient K_d, defined as

K_d = mols of cation per gram of resin/mols of cation per ml of solution.

Thus for K_d=1, there are equal molar amounts of the cation in one gram of resin and in one milliliter of solution. In very dilute solutions of hydrochloric acid, for instance, the distribution coefficients are close to 1000 but drop rapidly to between 10 and 1 for acid concentrations greater than

4 $\underline{M}$. This behavior is found also in nitric acid solutions and in sulfuric acid solutions. As acid concentrations are increased above 4 $\underline{M}$, the distribution coefficients drop dramatically. This effect can be explained as a competition between the complexing or active sites on the resin and the complexing anions in solution for the plutonium cations. As the concentration of complexing anions in solution becomes greater, plutonium cations are pulled back from the resin into the solution. This effect is not found in perchloric acid solutions because perchlorate anion is thought to have little or no complexing attraction for plutonium cations. In fact, as the perchloric acid concentration is increased above 5 $\underline{M}$, the distribution coefficient is increased quite rapidly. (Working with concentrated perchloric acid solutions and organic ion exchange resins could be hazardous because explosive organic perchlorates may be formed.) Distribution coefficients for neptunyl ions and uranyl ions are much lower than those for plutonium. Thus, mixtures of plutonium and uranium or neptunium can be absorbed onto cation resins from weak acid solutions and then selectively eluted from the resin column by careful control of the strength of the eluting acid, which will cause the uranium or neptunium to be removed from the resin while the plutonium is still retained on the column.

Cation exchange resin separations are also useful for separating plutonium from the transuranic actinide elements, or for separating plutonium from rare earth elements, the lanthanides. For the separation of plutonium from actinide element mixtures, two effective complexing agents are useful: ammonium lactate and ammonium α-hydroxy isobutyrate, described earlier in the section on complexing agents for

plutonium. When an actinide element mixture is absorbed on a cation resin, the individual actinide elements can be eluted separately with either 1 $\underline{M}$ ammonium lactate or 1 $\underline{M}$ ammonium α-hydroxy isobutyrate at a pH of 3.15. When mixtures of the lanthanides and plutonium are absorbed on an anion exchange resin, they can be separated by elution with 5 $\underline{M}$ ammonium thiocyanate. The plutonium is eluted first, then the lanthanides are eluted as a group. If more than one actinide element is present on the column, all of them will elute in the position where the plutonium elutes. This procedure does not separate individual actinides or lanthanides.

A more complex application of cation exchange resin separations is used to separate uranium, plutonium, and fission products into three fractions. This takes advantage of the very distribution coefficients for U (VI) and Pu (VI) in 10 $\underline{M}$ hydrochloric acid on cation resins. The sample mixture should first be treated with dilute perchloric acid by heating to fumes in order to ensure oxidation of the plutonium to Pu (VI). After cooling, the solution is applied to the top of the resin column, which has been pre-equilibrated with 10 $\underline{M}$ hydro-chloric acid. The column is then washed with additional 10 $\underline{M}$ hydrochloric acid to remove fission products, especially the lanthanides. Plutonium is removed from the column by washing it with a 10 $\underline{M}$ HCl–0.1 $\underline{M}$ HI mixture, which reduces the plutonium to the +3 oxidation state, which has a very low distribution coefficient in this system. The uranium is the last to be removed, which is done by washing the column with 0.1 $\underline{M}$ hydrochloric acid, under which

condition the distribution coefficient for U (VI) is low. It is best to use 10% cross-linked resin for this procedure.

Anion Exchange Resins

Anion exchange resins have proven to be very effective reagents for the purification of plutonium from nearly all other metal impurities, especially when it is desirable to recover the plutonium in dilute nitric acid with no other reagents present. Nearly all negatively charged plutonium complexes described earlier, especially the chloride and nitrate complexes, can be absorbed on anion exchange resins.

Among the three common plutonium species in hydrochloric acid solutions, only Pu (IV) and Pu (VI) are absorbed on an anion exchange resins such as Dowex 1. Pu (III) is not absorbed at any hydrochloric acid concentration, chiefly because it does not form a negatively charged chloride complex. Pu (IV) is absorbed at hydrochloric acid concentrations greater than 2 $\underline{M}$, while Pu (VI) is absorbed at concentrations greater than 6 $\underline{M}$. The Pu (VI) species can be eluted from the resin by washing with 3 $\underline{M}$ hydro-chloric acid, and the Pu (IV) is removed by washing with 1 $\underline{M}$ acid. This affords a method for separating the two species, although steps must be incorporated into the separation procedure to avoid reducing the Pu (VI) to Pu (IV) while it is being absorbed into the resin or being eluted from it. Inasmuch as U (VI) is also absorbed from hydrochloric acid solutions that are 6 $\underline{M}$ or greater, the use of an anion exchange resin affords a method for separating Pu (IV) and U (VI). Reaction rates between the resin and

the solutions are greatly dependent on temperature and cross linkage (assuming uniform resin bead size). Rates of absorption and desorption are slow for high cross linkages such as 10% or 12%, but rapid for 2% cross linkages. Elution of the plutonium from the resin with low hydrochloric acid concentrations, less than 1 $\underline{M}$, are rapid when the column and the desorption solution are heated to 65ºC. For low milligram amounts of plutonium and small columns, use of a graded 100–200 mesh resin will produce good results in a reasonable time. Smaller mesh sizes (200–400 mesh) will cause considerably longer times for the solutions to travel through the column.

Nitric acid systems provide the most effective method for the purification of plutonium from most impurities. This high degree of effectiveness exists because very few metal cations form negatively charged nitrate complexes. Only those that possess a +4 oxidation state, and even then only cerium, zirconium, and thorium complexes have as high a stability constant as does plutonium in its +4 oxidation state. The plutonium complex absorbed by anion resins such as Dowex 1 is the hexanitrato complex, $Pu(NO_3)_6^{2-}$, which has a distribution coefficient greater than 3000 in 7.5 $\underline{M}$ nitric acid at room temperature. The anion resin used in this case is Dowex 1-X2. Higher concentrations of nitric acid show slightly smaller distribution coefficients, probably because of the formation of $HPu(NO_3)_6$, which is not as strongly absorbed as the hexanitrato complex.

The recommended procedure for the purification of milligram or microgram amounts of plutonium is based on the use of the $Pu(NO_3)_6^{2-}$ complex, as follows. Place the plutonium aliquot, preferably less than a milliliter, in a 10-ml beaker and evaporate it to a small volume, but not to dryness, under a heat lamp. Remove the beaker from the heat lamp, add 1 or 2 drops of 1 $\underline{M}$ hydroxyl-amine nitrate and allow it to stand for ten minutes to reduce all of the plutonium to Pu (III). Then add 2 drops of 2 $\underline{M}$ potassium nitrite, which will oxidize all the plutonium to Pu (IV). Add 1 ml of 8 $\underline{M}$ nitric acid to the beaker and transfer drops of the solution to the top of a resin column, 0.3 mm wide by 5 cm long. The anion exchange resin should be graded Dowex 1-X2 that has been previously washed with 7.5 $\underline{M}$ nitric acid. A band of green will appear at the top of the resin column, which indicates the location of the absorbed plutonium. Carefully wash the resin column without disturbing the green band, with at least six separate portions of 7.5 $\underline{M}$ nitric acid, or until the alpha count rate in the eluate drops to a small or negligible value. This removes the impurities, especially americium, which is present in all unpurified plutonium solutions. Heat the column with an infrared heat lamp, and wash the column carefully with 0.1 $\underline{M}$ nitric acid that has been heated in a boiling water bath. All of the plutonium should be eluted in less than a ml of the dilute acid. Add 2 drops of concentrated nitric acid to the plutonium fraction to prevent hydrolysis.

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CHAPTER 10

RADIOACTIVITY AND ITS PRESENCE IN NATURE

Radioactivity is an ever-present part of our natural environment. The atoms of some isotopes of the chemical elements are unstable and change over the course of time into either unstable or stable atoms of other elements. The unstable atom emits a charged particle from its nucleus as it changes to the new atom. The emission of these charged particles from a collection of the unstable atoms is called radioactive decay, whose discovery is described in the first part of this book. This means that the original unstable nucleus, A, "decays" to a different nucleus, B, of a different chemical element. The rate of emissions from a collection of radioactive nuclides is known as the disintegration rate and is usually referred to as disintegrations per second (d/s) or disintegrations per minute (d/m). Some kind of a radiation detector is used to measure the disintegration rate by means of the ionization created by the charged particles as they pass through matter. The measurement actually detects only part of the total radiation because the detectors used are not 100% efficient. This results in measured counts per second (c/s) or counts per minute (c/m), whose value is less than the actual disintegration rate because of the counting device's efficiency being less than 100%.

The distinction between the disintegration rate and the measured count rate is important. The disintegration rate is an intrinsic property of the radioactive nuclide and is a number that is calculated from the half-life of the nuclide; it is a number that is unique for that nuclide. The measured count rate of a collection of radioactive atoms depends solely on the number of atoms of that isotope in the collection and the efficiency of the detector used to measure the count rate. As an example, Pu-239 has a half-life of 24,120 years; its disintegration rate, calculated from the half-life, is approximately 137,700 d/m per microgram of isotope. When 0.1 microgram of the isotope is placed in a detector that has 51% efficiency, the measured count rate will be 137,700 x 0.1 x 0.51 = 7023 c/m.

The distinction between disintegration rate and count rate is important when describing the activity of radioactive nuclides. As just mentioned, the disintegration rate is difficult to measure directly because very few detection systems are able to measure all of the disintegrations from a radioactive nuclide. This is because very few detection instruments can be designed and used for detection of the entire radioactivity without incurring extra cost and sacrificing ease of use. The disintegration rate of a radioactive nuclide, however, is easily calculated from its half-life, as will be described in a later chapter. Measuring the count rate, instead of the disintegration rate, of a collection of radioactive nuclides, is much simpler and cheaper and can be done with good precision. Such a measurement can be converted to a calculated disintegration rate for the measured sample by correcting the count rate for the efficiency of the detector, which is usually not much more than 50%. Thus if a Pu-239 sample has a count rate of 70,230 c/m, and the detector's efficiency is 51%, dividing 70,230 by 0.51, gives a value of 137,700 d/m, which is the disintegration rate for 1 microgram of Pu-239.

Naturally Occurring Radioactivity

Examples of naturally occurring radioactive isotopes are potassium-40, an isotope of the potassium that is found in the crust of the earth and in plants and animals, and carbon-14, which is continuously generated in the atmosphere by cosmic rays. A certain fraction of potassium-40 decays to stable calcium-40, while the remainder decays to argon-40, a stable isotope of the rare gas argon. Carbon-14 decays to stable nitrogen-14. Since carbon and potassium are present in animals and plants, all living organisms exhibit a small amount of radioactivity. In humans, the disintegration rate for these two radioactive nuclides is between 100,000 and 200,000 d/m, depending on the person's weight. These two radioactive nuclides are listed in Table 10-1, which shows all of the naturally occurring radioactive isotopes and elements. (Note – Potassium-40 contributes an activity of 300 pCi/liter in seawater).

Table 10-1.
Naturally Occurring Radioactive Nuclides

Nuclide	Half-Life (years)	Activity of Element (d/m/gram)	Element Abundance*
U-238	4.5×10^9	1,500,000	2×10^{-6}
U-235	7.0×10^8	1.4×10^{-8}	2.5×10^{-5}
Th-232	1.4×10^{10}	244,000	6×10^{-6}
Pt-190	6×10^{11}	70	1×10^{-8}
Os-186	2×10^{15}	3	2×10^{-10}
Re-187	4.5×10^{10}	59,000	4×10^{-10}
Ta-180	$>1.2 \times 10^{15}$	<1	2×10^{-6}
Hf-174	2.0×10^{15}	<1	4×10^{-6}
Lu-176	3.6×10^{10}	3,200	8×10^{-7}
Gd-152	$1.1 \text{ c } 10^{14}$	<1	6×10^{-6}
Sm-149	7×10^{15}	<1	7×10^{-6}
Sm-147	1×10^{16}	<1	7×10^{-6}
Nd-144	2×10^{15}	<1	4×10^{-5}
La-138	1×10^{11}	5	5×10^{-5}
Te-123	$>1.3 \times 10^{13}$	<1	2×10^{-9}
In-115	4.4×10^{14}	15	2×10^{-7}
Cd-113	9×10^{15}	<1	2×10^{-7}
Rb-87	4.5×10^{10}	57,000	7×10^{-5}
V-50	1×10^{17}	<1	2×10^{-4}
K-40	1.3×10^9	1800	1.68×10^{-3}
C-14 (!)	5.74×10^3	-	
Be-7 (!)	0.15		
H-3 (!)	12.3	-	

* grams per million grams in the earth's crust
(!) continuously formed in the atmosphere by cosmic rays

The carbon and potassium isotopes described above are examples of radioactive isotopes of elements whose other isotopes are stable. There are other elements that are also mostly composed of stable isotopes and one or two radioactive isotopes. These are found in the periodic table all the way from hydrogen to platinum, and are listed in Table 10-1. All of these radioactive isotopes, which occur naturally, have long half-lives, with the exception of hydrogen-3, beryllium-7 and carbon-14. Most of the half-lives correspond to disintegration rates that are less than 1000 d/m for a single gram of the whole element, and the detection of their radioactivity requires specially designed instruments.

A second class of radioactive elements in nature is found among the very elements in the periodic table. These are thorium and uranium, the two elements that led to the discovery of radioactivity; they have no stable isotopes. Thorium has only one naturally occurring isotope, radioactive Th-232. Uranium is composed of U-235 and U-238. A third uranium isotope, U-234, is present in uranium only as the result of a decay chain that starts with U-238.

The three nuclides U-238, U-235, and Th-232 are the precursors, or parents, of three series of radioactive decay chains, each composed of approximately ten radioactive nuclides that are found in ores of the two elements. Two of the nuclides, Th-232 and U-238, have half-lives of 14 billion years and 4.5 billion years, respectively, equal to or greater than the age of the earth, 4.6 billion years. The third nuclide, U-235, has a half-life of 700 million years, or about one-sixth the age of the earth. The magnitude of these half-lives means that practically all of the thorium present at the formation of the earth still exists, about half that of U-238 still exists, and a little less that one-sixth of the original U-235 still exists. Since U-235 comprises only 0.72% of the element uranium, it can be said that half of the original uranium still exists on earth.

The precursors, or parents, of the naturally occurring radioactive chains, U-238, U-235, and Th-232 are shown in Table 10-1, along with other radioactive nuclides that occur naturally in the earth's crust. (U-234 is a member of the chain whose parent is U-238). The last three entries in Table 10-1, C-14, Be-7, and H-3, known as tritium, are continuously generated in the atmosphere by nuclear reactions involving cosmic rays. They all reach stability with a single decay. The thorium decay chain and the two uranium decay chains are formally designated as the 4N chain (Th-232), the 4N+2 chain (U-238), and the 4N+3 chain (U-235). These formal designations are based on division by 4 of the mass number of a chain member. Thus, 238 divided by 4 leaves a remainder of 2 so that U-238 is a member of the 4N+2 chain. The mass number 235 when divided by 4 leaves a remainder of 3, so that U-235 belongs to the 4N+3 chain. The members of the 4N chain all have mass numbers that are divisible by 4 with no remainder. The 4N+1 chain does not occur naturally because its longest lived member, Np-237, has a half-life of 2.1 million years, which is short compared to the earth's age of 4.6 billion years. Whatever Np-237 existed at the time of the formation of the earth has decayed to practically nothing, and it can be classed as an extinct element in the earth's crust. It exists currently, however, because it is produced in significant quantities from Pu-241, which is made in nuclear reactors.

Decay Modes of the 4N+x Series

The members of the three naturally occurring radioactive decay chains, 4N, 4N+2, 4N+3, and the artificially created chain, 4N+1, all exhibit two decay modes, (1) alpha particle decay (α) and (2) beta particle decay (β). Alpha particle decay results in the ejection of an alpha particle from the nucleus, with a corresponding mass number change from N to N-4 because the alpha particle is a helium nucleus with a mass number of 4. Since the ejected helium nucleus, or alpha particle, also has a charge of +2, the daughter nucleus not only has its mass number decreased by 4, but has its nuclear charge decreased by 2. Therefore, alpha particle decay of an atom always produces a daughter atom whose mass number is 4 less than its parent's mass, and whose nuclear charge, or atomic number, is 2 less than its parent. The alpha particle decay of a U-238 atom, whose nuclear charge is +92 and whose atomic number is 92, produces a Th-234 atom with a mass number of 234 and a nuclear charge of +90. The alpha particle decay of Pu-239, whose nuclear charge is +94 and whose atomic number is 94, produces an atom of U-235, with a charge of +92, and an atomic number of 92. It is common practice not to have to specify the plus sign for the nuclear charge; the atomic number and the nuclear charge of an atom are specified by the same signless number. This is permissible because all atoms have positive nuclear charges.

On the other hand, beta particle decay consists of the ejection of a negatively charged electron from the atomic nucleus. The mass of the electron is quite small compared to that of the helium nucleus, nearly 7500 times lighter, so that the mass change is negligible, and the mass number of the parent and daughter atoms is the same. Since the ejection of the beta particle carries away an electrical charge of -1, the charge on the nucleus is increased by +1, and the atomic number increased by 1. The Th-234 daughter of U-238, mentioned above, is a beta particle emitter. Its daughter atom has a mass number of 234, unchanged from the parent Th-234, but with a nuclear charge and atomic number of 91, an increase of 1 from the charge and atomic number of 90 for Th-234. Element 91 is protactinium, whose symbol is Pa.

The decay schemes of the three naturally occurring chains and the one artificially produced chain are shown in Figures 10-1, 10-2, 10-3, and 10-4. The mass number of each nuclide is shown as a prefix superscript, which is the preferred way when writing nuclear reactions. The decay mode, α or β, is shown above the arrow depicting the decay from parent to daughter, and the half-life is shown beneath the arrow, where the abbreviations are y = years, d = days, m = minutes, ms = milliseconds, and μs = microseconds. (Some published charts of the nuclides use a = annum instead of y = years).

There are several interesting features about these decay paths. All three of the naturally occurring series end with the production of the three stable lead isotopes, Pb-206, Pb-207, and Pb-208. This accounts for all of the stable lead atoms found in the earth's crust, aside from that formed by nucleosynthesis in the supernova explosion that supplied the material for the formation of our solar system. The one artificial decay series, 4N+1, ends with the production of the only stable bismuth isotope, Bi-209. The three naturally occurring series all contain isotopes of elements that are found in the earth's crust, and no others. The artificial

series contains two elements not known in the earth's crust, astatine and francium, in addition to isotopes of known elements. All four series contain nuclides with very short half-lives on the order of microseconds or less. One series, the 4N series, shows a significant branching (64% and 36%) in the Bi-212 decay. The other three also exhibit branching between alpha and beta decay modes, but only to the extent of 2% or less, so these branches have not been shown. Wherever such branching occurs, the two paths always come together before the end of the chain is reached.

Because of the existence of these naturally occurring decay series, ores of thorium and

uranium found in the earth are much more radioactive per gram of ore than either the pure thorium or uranium. All uranium ores such as pitchblende and uraninite contain all three uranium isotopes, U-238, U-235, and U-234, the latter being a daughter of U-238. In addition, because the ores are many millions or a few billion years old, the two decay chains, 4N+2 and 4N+3, have had sufficient time for all members of each chain to reach an equilibrium state. This means the disintegration rate of each daughter is equal to the disintegration rate of its parent. This is sometimes referred to as secular equilibrium, alluding to the fact that the primary parent, U-239, U-235, or Th-232, does not change in

^{238}U $\xrightarrow{\quad\alpha\quad}$ ^{234}Th $\xrightarrow{\quad\beta\quad}$ ^{234}Pa $\xrightarrow{\quad\beta\quad}$ ^{234}U $\xrightarrow{\quad\alpha\quad}$ ^{230}Th $\xrightarrow{\quad\alpha\quad}$
4.51 E9 y   24.1. d   1.2 m   2.46 E5 y   7.54 E4 y

^{226}Ra $\xrightarrow{\quad\alpha\quad}$ ^{222}Rn $\xrightarrow{\quad\alpha\quad}$ ^{218}Po $\xrightarrow{\quad\alpha\quad}$ ^{214}Pb $\xrightarrow{\quad\beta\quad}$ ^{214}Bi $\xrightarrow{\quad\beta\quad}$
1590 y   3.8 d   3.1 m   27 m   19.9 m

^{214}Po $\xrightarrow{\quad\alpha\quad}$ ^{210}Pb $\xrightarrow{\quad\beta\quad}$ ^{219}Bi $\xrightarrow{\quad\beta\quad}$ ^{210}Po $\xrightarrow{\quad\alpha\quad}$ ^{206}Pb (stable)
164 ms   22.6 y   5.01 d   138 d
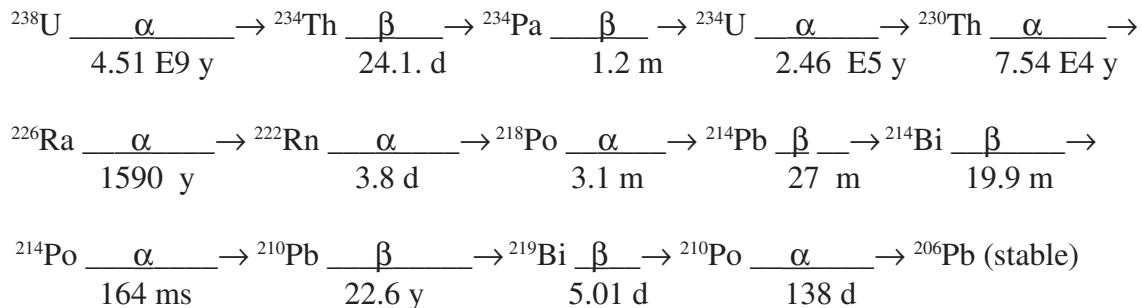
Fig. 10-1. U-238 Decay Series (4N + 2)

^{235}U $\xrightarrow{\quad\alpha\quad}$ ^{231}Th $\xrightarrow{\quad\beta\quad}$ ^{231}Pa $\xrightarrow{\quad\alpha\quad}$ ^{227}Ac $\xrightarrow{\quad\beta\quad}$ ^{227}Th $\xrightarrow{\quad\alpha\quad}$
7.04 E8 y   1,06 d   3.28 E4 y   21.8 y   18.7 d

^{223}Ra $\xrightarrow{\quad\alpha\quad}$ ^{219}Rn $\xrightarrow{\quad\alpha\quad}$ ^{215}Po $\xrightarrow{\quad\alpha\quad}$ ^{211}Pb $\xrightarrow{\quad\beta\quad}$ ^{211}Bi $\xrightarrow{\quad\alpha\quad}$
11.4 d   3.96 s   1.78 ms   36.1 m   2.14 m

^{207}Tl $\xrightarrow{\quad\beta\quad}$ ^{207}Pb (stable)
4.77 m
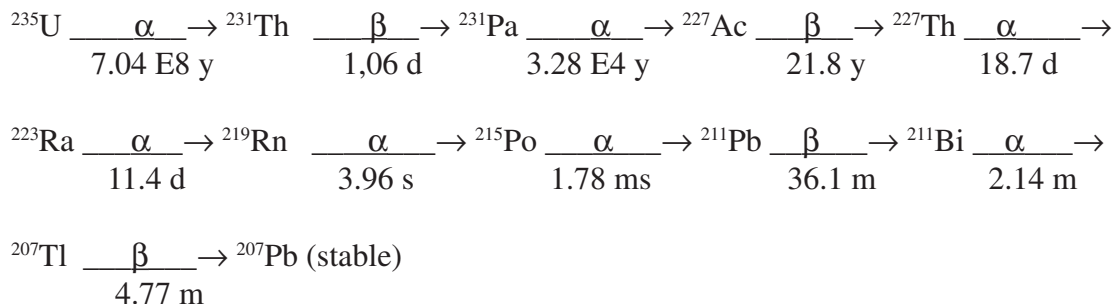
Fig. 10-2.   U-235 Decay Series (4N + 3)

^{232}Th ____α____→ ^{228}Ra __β__→ ^{228}Ac __β____→ ^{228}Th ___α____→ ^{224}Ra ____α___→
        1.40 E0 y   5.76 y   6.15 h   1.91 y   3.66 d

^{220}Rn ____α____→ ^{216}Po __α____→ ^{212}Pb ____β____→ ^{212}Bi ___β___→ ^{212}Po
        3.66 d   1.145 s   10.6 h   1.01 h   (64%)

                                                      α │ (36%)   α │ (36μs)

                                                      ▼   ▼
                                        ^{208}Tl _____β_____→ ^{208}Pb (stable)

Fig. 10-3. Th-232 Decay Series (4N)

^{237}Np ___α___→ ^{233}Pa ___β___→ ^{233}U ___α___→ ^{229}Th ___α___→ ^{225}Ra __β__→
        2.14 E6 y   27.0 d   1.59 E5 y   7340 y   14.9 d

^{225}Ac ____α___→ ^{221}Fr ___α___→ ^{217}At ___α___→ ^{213}Bi __β___→ ^{213}Po __α___→
        10.0 d   4.8 m   32 ms   45.6 m   4 μs

^{209}Pb ___β___→ ^{209}Bi (stable)
        3.2 h

Fig. 10-4. Np-237 Decay Series (4N + 1)

a detectable amount from century to century because of their very long half-lives. (It might have been called "everlasting" equilibrium). Starting with pure U-238, it requires about 1.78 million years to reach 99% of equilibrium, where all of the daughter nuclides are present to within 1% of their equilibrium, or steady state, numbers. If no geological processes have taken place that would selectively remove a relatively long-lived member of the chain, thus interrupting the attainment of equilibrium, all members will be present at their maximum quantities in the ore at the time it is mined. In the case of the U-235 decay chain, 99% of equilibrium is reached in 220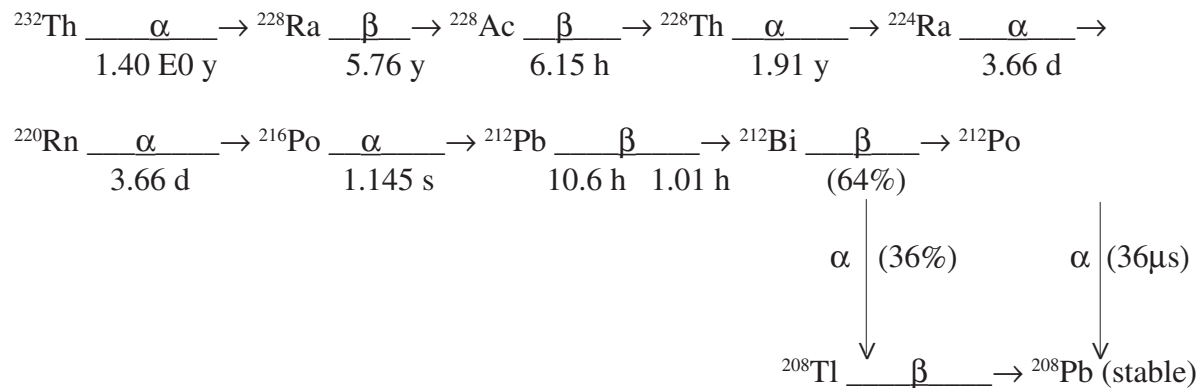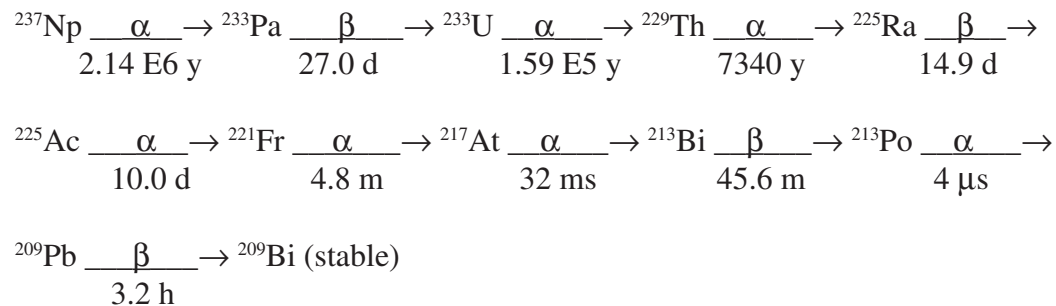,000 years, and in the case of the Th-232 chain, 99% of equilibrium is reached in 39 years. This means that in the case of the Th-232 chain, equilibrium is restored to 99% in 39 years after the decay chain is interrupted by a geologic process or by purification of the thorium. The reason for the differences in the time to reach 99% of equilibrium in these three natural decay chains is the presence or absence of a long-lived daughter in the chain.

The two uranium chains contain long-lived daughters, while the thorium chain has no daughter with a half-life greater than a bit more than 5 years.

The attainment of equilibrium in these three chains increases the radioactivity of these ores by a factor of eight or more. Counting up the total number of separate alpha and beta decay steps, it becomes clear that an ore of uranium will exhibit alpha radioactivity seven or eight times that of the parent U-238 or U-235. Once the uranium is extracted in pure form, it only exhibits the characteristic radioactivity of the pure element. The same can be said for thorium ores, with one significant difference. The next-to-last member of the 4N chain, TL-208, besides emitting a beta particle, also emits one of the most penetrating gamma rays found in nature, approximately 2.6 MeV. The detection of this gamma ray is a very good index for the presence of thorium ores.

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CHAPTER 11

RADIATION PROPERTIES OF THE COMMON PLUTONIUM ISOTOPES

Isotopes from Nuclear Reactors

The element plutonium, whose symbol is Pu, is the 94th element in the periodic table, which means it has a nuclear charge of +94, also known as the atomic number, denoted by Z. The element is not found in the earth's crust because none of its isotopes, except possibly one, has a half-life long enough to have survived since the formation of the solar system 4.6 billion years ago. Nearly all of the plutonium that exists today was made in nuclear reactors by bombarding natural uranium-238 with neutrons. A few of the rarer isotopes of plutonium have been produced by other kinds of nuclear reactions.

The common plutonium isotopes and their modes of production in a nuclear reactor are listed in Table 11-1. The notation used in the mode description is standard for describing the production of nuclides by nuclear reactions. The most complicated path is that for Pu-238. It is produced in a nuclear reactor by the (n,2n) reaction, in which one neutron is absorbed by the nucleus, and two are emitted. This reaction in a U-238 atom produces a U-237 atom, which has a short half-life of 5 hours and decays by beta particle emission to Np-237. The long-lived Np-237 becomes a target nucleus for an (n,γ) reaction, which creates Np-238, which has a short half-life and decays by beta particle emission to Pu-238. Notice that the absorption or emission of neutrons does not change the charge on the nucleus (Z), so that the chemical element is not changed in such reactions. The emission of a beta particle, however, increases Z by 1 because the beta particle emission removes a negative charge from the nucleus. The new nucleus now has a positive charge of Z+1, which is the nucleus of the next higher element. Nearly all of the neutron absorption reactions that do not result in the emission of a charged particle are quickly followed by gamma ray emission, hence the use of the (n,γ) notation. When a Pu-239 atom is made, the U-238 target nucleus first absorbs a neutron, forming the short-lived U-239 nucleus. This then decays with beta particle emission to form Np-239, which is also short-lived and decays by another beta particle emission to the long-lived Pu-239 nucleus.

Thus starts the production of the plutonium isotopes in a nuclear reactor. Since all of the plutonium isotopes have half-lives of more than several years (except

Table 11-1.
Production Modes of Some Plutonium Isotopes

Isotope	Mode	Half Life
Pu-238	Reactor - U-238 (n ,2n), U-237 (β), Np-237 (n,γ), Np-238 (β)	87.7 y
Pu-239	Reactor - ^{238}U(n, γ, 2β)	24,120 y
Pu-240	Reactor - ^{239}Pu(n, γ)	6570 y
Pu-241	Reactor - ^{240}Pu(n, γ)	14.3 y
Pu-242	Reactor - ^{241}Pu(n, γ)	387,000 y
Pu-243	Reactor - ^{242}Pu(n, γ)	5 h
Pu-244	Supernova Element Synthesis	8.0×10^7 y

Pu-243), the atoms of each isotope remain in the reactor long enough to be targets for further (n,γ) reactions, the process for producing the isotopes up to Pu-242. Each higher isotope is made at the expense of the lower one. This process essentially stops with the production of Pu-243 because this nuclide has a short half-life of 5 hours and is not present long enough to form significant quantities of Pu-244 in the reactor fuel. Other methods are required to produce Pu-244 in the laboratory for research purposes.

Some of the properties of the plutonium isotopes produced in a nuclear reactor from U-238 fuel are summarized in Table 11-2. (Fission neutrons from the small amount of U-235 maintain the nuclear chain reaction and provide neutrons for the plutonium production.)

The abundances for the plutonium isotopes are typical of plutonium produced in a reactor similar in design to the original Hanford reactors. The abundances may be different for reactors that follow the design of the Savannah River reactors. It is desirable that the amount of Pu-240 be less than about 5%, and this is controlled by the burnup of the U-238 in the production reactor. The burnup depends on the neutron flux in the reactor and the length of time the uranium fuel rods remain in the reactor. Larger proportions of Pu-240 are undesirable for use in weapons because spontaneous fission in Pu-240 is much greater than in Pu-239. Too

much Pu-240 can cause decreased explosive efficiency in a nuclear weapon. In the case of electrical power reactors the burnup can be allowed to proceed to where the Pu-240 content can climb as high as 20% or 40%, but such plutonium is not very suitable for use in high-efficiency nuclear weapons.

The other isotope of interest in Table 11-2 is Pu-241. This is the only plutonium isotope in the table that is not an alpha particle emitter. It decays by beta particle emission to Am-241, which is an alpha emitter that decays to Np-237, the longest lived nuclide in the 4N+1 series. The beta particles from Pu-241 are very low in energy and difficult to detect. They are not observed in the conventional alpha particle detectors used for measurement of the radioactivity of plutonium. The Pu-241 is regarded as a "nuisance" isotope because it is responsible for the continuous growth of increasing amounts of Am-241 in plutonium, thus serving as a source of an impurity. For plutonium containing 0.3% Pu-241, this growth of americium impurity amounts to about 0.015% by weight per year. This apparently small amount is significant because Am-241 alpha particle decay is accompanied by a 60 keV gamma ray in 70% of the alpha decays. This can lead to a gamma ray exposure hazard to workers handling multigram amounts of aged plutonium. The repurification of plutonium leads to significant amounts of Am-241 in the waste streams from the purification

Table 11-2.
Properties of Reactor Produced Plutonium Isotopes

Isotope	Half - Life	Decay Mode	Typical Abundance	Daughter
Pu-238	87.7	Alpha	0.01%	U-234
Pu-239	24,120	Alpha	95.	U-235
Pu-240	6570	Alpha	4.8	U-236
Pu-241	14.3	Beta	0.3	Am-241
Pu-242	387,000	Alpha	<0.01	U-238

process. Small amounts of Am-241 are used in smoke detectors for domestic purposes.

The radioactive decay of the plutonium isotopes leads to the introduction of impurities in initially pure plutonium. Table 11-3 summarizes the proportions of impurities that grow into plutonium in one year. The initial plutonium isotopic composition represents the nominal weapon grade variety, not that which would be produced in a power reactor. Growth of the impurities into plutonium from a power reactor would be much faster and in different proportions since the plutonium isotopes heavier than Pu-239 are present in much higher ratios in power reactor plutonium. All of the isotopes produce uranium impurities except for Pu-241, which is the only plutonium isotope in reactor-produced plutonium whose decay does not produce a uranium isotope.

A special problem with daughter in-growth is found in the case of highly enriched Pu-238, which is used as a heat source in some applications. Because the half-life is relatively short for this isotope, 87.7 years, the loss of plutonium by decay and the production of U-234 from the same decay cause a measurable decrease in the amount of plutonium, about 0.71% per year.

The Pu-244 Story

Although Pu-244 is not found in reactor-produced plutonium, it has been found in debris from thermonuclear weapon tests. It is included in the table because of its importance in studies related to the age of the solar system. Searches have been made for Pu-244 in the crust of the earth since 1960, but strong evidence for its present-day existence has not been confirmed. Astrophysicists believe that Pu-244 was a member of all the nuclides present at the beginning of the solar system. These primordial nuclides, which included all of those presently known, were probably formed in a supernova explosion of a massive star, which evolved after the origin of the universe, according to the "big bang" theory, some 15 billion years ago. The supernova explosion created the elements heavier than Fe-56, which is the highest Z nuclide that can be produced in the helium burning stage of a star, according to current astrophysical theory. If such a star burns all of its helium, eventually forming a core of iron, and it is more than 10 times the mass of our sun, it will collapse under the force of its gravity. This leads to temperatures so high and densities so great that nuclear reactions occur very rapidly, producing elements heavier than iron and forming transuranium elements and others even heavier. This stage

Table 11-3.
Impurities in Plutonium from Decay Products in One Year

Pu Parent	Parent %	Daughter Impurity	ppm Daughter
Pu-238	0.01	U-234	0.8
Pu-239	95.	U-235	28
Pu-240	4.5	U-236	5
Pu-241	0.3*	Am-21	142*
Pu-242	<0.1	U-238[8]	<0.002

*Pu-241 in aged plutonium from dismantled weapons is less abundant because of its short half-life.

terminates in a supernova explosion that scatters the massive star's material into the surrounding galaxy. This scattered debris becomes material for the formation of new stars and planets. Thus, our solar system, which is at least a second-generation system, contained many super-heavy elements that are now extinct because of having half-lives that were short in comparison with the 4.6-billion-year age of our solar system. Plutonium-244 is one of these extinct elements. Some astrophysicists estimate that at the beginning of the solar system, Pu-244 may have had an abundance of 1 atom for every 10 atoms of U-238 that then existed.

In addition to its alpha decay mode, Pu-244 has a significant probability for spontaneous fission, and these fission tracks are found in some of the oldest meteorites on earth and rocks on the moon. The fact that these fission tracks came from Pu-244 is confirmed by the mass ratio of xenon isotopes found in the stony meteorites and lunar rocks, since these ratios could only result from the fission of Pu-244. Its half-life of 80 million years is short compared to the age of the solar system, 4.6 billion years, and the nuclide has virtually disappeared from the earth's crust as a result of radioactive decay. Its daughter, U-240, rapidly decays to Np-240, which rapidly decays to Pu-240. Over tens of thousands of years this decays to U-236, which decays with a half-life of

23 million years to the very long-lived U-232, still found in the crust of the earth.

Heat From Radioactive Decay

As noted earlier, alpha particle emission creates heat in the alpha particle source and in any inert material surrounding the source that is within the range of the alpha particles. Thus, plutonium materials are a source of heat. Table 11-4 shows how the different plutonium isotopes vary in their heat output. The decay of plutonium, whether by alpha particle emission or by beta particle emission, produces heat in the material containing them. The temperature increase can be significant, depending on the abundance of the individual isotopes present in the material. The range of an alpha particle in most solid materials is less than 0.01 mm, which means the alpha particle will be completely stopped within the material. The absorbed energy of each alpha particle is converted to heat in the substance that stops it. This temperature rise will be dependent on the amount of plutonium present since the amount determines the rate of alpha particle emission. This energy release or heat effect is measured in watts per gram of plutonium.

The perceptible temperature increase, of course, depends not only on the amount of plutonium in the material, but also on the

Table 11-4.
Heat Generation by Plutonium Isotopes

Isotope	Half - Life	Watts per kg.	Particle Energy (meV)	
Pu-238	87.7	560.	α	5.50, 5.46
Pu-239	24,120	2.	α	5.16, 5.15, 5.11
Pu-240	6570	7.5	α	5.17, 5.12
Pu-241	14.3	13	β	0.02 (max)
Pu-242	387,000	0.11	α	4.123

volume of the material. Pure plutonium metal containing the isotopic proportions shown in Table 11-2 will feel warm to the touch if the metal weighs more than 50 grams. The same amount dissolved in a liter of solution has to disperse the heat energy through 1000 grams of solution, and the temperature rise will be slight. For plutonium-238, which generates nearly 0.5 watt per gram, a 1-gram metal source will feel warm, and a 10-gram source will feel hot. A 250-gram plutonium oxide source, in the form of a sphere and containing a little more than 200 grams of Pu-238, will be hot enough to glow in the dark.

Particle Emission Energy

The last column in Table 11-4 lists the energy of the emitted particle, whether alpha or beta. In the case of the alpha particle emitters, there are at least two values shown, fairly close to one another for a particular isotope. The most energetic value is the energy to the alpha particle emitted when the atom decays to the "ground" state of its daughter atom. For instance, in the case of Pu-239, the value of 5.16 MeV is the particle energy for this ground state transition, and that's the only radiation energy that will be observed. There are two other energies listed, however, 5.15 and 5.11 MeV. Decays that result in the emission of alpha particles with these two energies will be followed immediately by gamma ray emission from the U-235 daughter atom. For the 5.15 MeV alpha particle emission, the gamma ray will be approximately 0.01 MeV, while for the 5.11 MeV alpha particle emission, the gamma ray from the U-235 daughter atom will be approximately 0.05 MeV. In these two latter cases, the decay of the Pu-239 atom leads to an "excited" state of the U-235

atom, which undergoes deexcitation by the emission of a gamma ray, usually within a very short time. The sum of the alpha particle energy and its associated gamma ray energy is equal to the energy of the ground state decay, which in this case is 5.16 MeV. When the gamma ray spectrum of plutonium-239 is examined in detail, however, many more gamma rays of higher energies are seen. These result from alpha particle decays to higher excited levels in the U-235 atom, but in such low fraction of the total decay events over a period of time that the energies of the corresponding alpha particles are difficult to measure. They are essentially hidden in the sea of 5.16, 5.15, and 5.11 MeV alpha particles as a result of the limitations in the alpha particle detector. High-resolution gamma ray detectors do not suffer from these effects and will detect gamma rays of several hundred different energies from Pu-239 decay, some with energies greater than 0.8 MeV. The abun-dance of these decays, with respect to the total number of decays in a given time, becomes quite low as the gamma ray energy increases. Gamma rays from a particular daughter nuclide are in most cases unique for that nuclide and are therefore useful for the identification of the nuclide, as is also the measurement of the alpha particle energy of the nuclide.

The single beta particle emitter in Table 10-4, Pu-241, does not exhibit the multiple, discrete emission energies that are found in alpha particle decay. The value its beta particle energy, 0.02 MeV, represents is that maximum value observed. The beta particles from this plutonium isotope can have energies all the way from close to zero to the maximum energy, with a continuous abundance distribution that drops off gradually to a low value at the maximum.

Again, the maximum value represents the decay transition to the ground state of the daughter, Am-241, but unlike in the case of alpha particle emission, there are no discrete gamma rays associated with these beta particles, which can have nearly any energy equal to or less than 0.02 MeV. The beta particles with energies less than 0.02 MeV represent transitions where the excess energy is carried off by neutrinos. Since neutrinos have no charge and extremely low or undetectable mass, they are not found by common instrumental techniques in the laboratory.

CHAPTER 12

DETECTION AND MEASUREMENT OF PLUTONIUM RADIATION

Alpha Particles

The alpha particles that are emitted by the common plutonium isotopes have energies between 5.10 and 5.50 MeV, except for Pu-241, which is primarily a beta particle emitter. These energies are in the lower part of the energy range of alpha particles emitted by the actinide nuclides that decay by alpha particle emission. These energies range from slightly more than 4 MeV to around 8 MeV. The plutonium isotopes that decay by alpha particle emission can all be detected and measured accurately by the well-known methods of radiation detection, such as gross alpha counting and alpha particle spectro-metry that will be described later.

The detection of alpha particles is based on the interaction between the alpha particle, which is a He^{2+} ion (helium nucleus), and the orbital electrons of the atoms in the material through which the alpha particles pass. The path of an alpha particle in air can be made visible in a device called a cloud chamber, and the path is seen as a straight line several centimeters long. The path is much shorter, although still straight, in liquids or solids because the densities of these materials are many times greater than that of air.

Atomic and Nucleon Sizes

All atomic nuclei are extremely small, somewhere between 1/5000 and 1/30,000 the size of their corresponding neutral atoms, whose size is on the order of 10^{-8} cm. and includes the expanse of their orbital electrons. An approximate relation between the radius of a nucleus and its atomic number is

$$R = kA^{1/3}, \qquad (12\text{-}1)$$

where R is the radius of the nucleus, assuming it has the shape of a sphere, A is the mass number, and k = 3 x 10^{-13} cm. Besides having a spherical shape, some nuclei may have the shape of a football or of a slightly flattened sphere, but for calculating an approximate radius for the nucleus, a spherical shape will be assumed. For a hydrogen atom, with A = 1, the radius of its nucleus is 3 x 10^{-13} cm. For a helium nucleus with A = 4, the nuclear radius is 4.8 x 10^{-13} cm., and for a uranium nucleus with A = 238, the nuclear radius is nearly 20 x 10^{-13} cm. Therefore, the range in the radius from the smallest nucleus to the largest is less than a factor of 7.

Interactions of Alpha Particles with Matter

Most of the mass of an atom is found in its nucleus, even in the lightest atom, hydrogen. In this case, the nucleus, a single proton, has a mass about 1800 times that of its single orbital electron. This combination of very small size and large relative mass leads to an extremely high density for the nucleus of any atom. The helium atom nucleus has a density of 10^{14} g/cc, and the uranium atom nucleus has a density of 10^{13} g/cc.

The facts of atomic size, nucleus size, and density lead to the conclusion that a neutral atom is mostly empty space. The picture that evolves is of a small, dense nucleus surrounded by electrons at distances that are many thousands times the size of the nucleus. In addition to this empty space within a neutral atom, there is also empty space between atoms or molecules in a gas

such as air. This space also plays an important part in the interaction of an alpha particle with matter. A cubic centimeter of air at standard conditions of temperature and pressure (STP) contains about 2.68×10^{19} molecules of nitrogen and oxygen. The cube root of this number therefore represents the average number of molecules along a line 1 cm. long, or about 3,000,000 molecules. This number of molecules in 1 cm results in an average distance between molecules of 1/3,000,000 cm, or about 3×10^{-7} cm. This distance between molecules is about ten times the diameter of either the nitrogen or the oxygen molecules in air at STP. Thus, in addition to the empty space within an atom, described above, there is even more empty space between the diatomic molecules of nitrogen and oxygen in air. When an alpha particle is emitted by a radioactive nuclide into air, it has a very low probability of striking another atomic nucleus, but a higher probability of striking an electron. The result of its colliding with another nucleus would be to deflect it through an angle from its original path because the target nucleus would most likely have a larger mass than the alpha particle. If it collided with an electron, the alpha particle would not be deflected measurably from its original direction because its mass is more than 7000 times the mass of the electron. The fact that visualization of alpha particle tracks by cloud chambers show straight lines means that a collision with another nucleus is a rare event for the passage of a single alpha particle through air.

In its passage through matter, whether a gas, liquid, or solid, the alpha particle is most likely to encounter an electron, which is knocked out of the way while the alpha particle continues on its original path. This ejected electron is now free to be attracted by

a positive electric field. The atom from which it was ejected now has a positive charge since it has lost an electron with a negative charge and is free to be attracted by a negative electric field.

An encounter between an alpha particle and an orbital electron of an atom is said to create an "ion pair", referring to the free negative electron and the more massive positive atomic ion. As the alpha particle continues its path through matter, it creates additional ion pairs. Each encounter transfers a small amount of energy from the alpha particle to an ion pair, and eventually the alpha particle comes to rest in the matter it has traversed. Since there are many free electrons near its stopping point, the double positive charge of the alpha particle attracts two free electrons so that it becomes a neutral helium atom.

As explained earlier, the most energetic Pu-239 alpha particle is 5.15 MeV. In its passage through air, each alpha particles transfers about 35 electron volts (eV) in each collision with an electron, to the resulting ion pair. If the absorbing matter is germanium, which is a common detector material, the energy release per collision is much less, about 2.9 eV per collision. Thus for an initial energy of 5.15 MeV, the alpha particle will produce about 147,000 ion pairs in air, and about 1.7 million ion pairs in germanium. In addition to this primary ionization caused by the alpha particle, the ion-pairs can produce secondary ionization if an electric field is present, as is the case in most gas or solid ionization detectors.

Range of Alpha Particles through Matter

The range of an alpha particle is the term used to describe the distance an alpha

particle will travel through an absorbing material before it comes to a "stop", having no more energy than the atoms in the absorber. The range, when expressed in centimeters, depends on (1) the initial energy of the alpha particle, and (2) the density of the absorbing material. When the absorber is a gas, its density is dependent on its temperature and pressure, and these latter two factors can affect the range when expressed in centimeters, often called the linear range.

Experimental studies of alpha particle absorption have developed a number of approximate relations for calculating the range of an alpha particle through pure elements and simple compounds. Another useful formula is Equation 12-2, which has the useful property that temperature and pressure are not needed for the calculation. In this equation, E is the initial energy of the alpha particle in MeV, and A is the mass number of the absorbing element in atomic weight units.

$$\text{Range} \, (\text{mg/cm}^2) = 0.173 E^{3/2} A^{1/3} \qquad (12\text{-}1)$$

If the absorber is thought of as a target consisting of a number of atoms per square centimeter without regard to their depth from the target surface, then the distance in depth between the atoms is immaterial. This target model collects all the atoms in a cubic centimeter of a target element and places them in a one-square-centimeter area that faces the oncoming alpha particles. The unit to express this is milligrams per square centimeter of the absorbing target element, and it is called the thickness range. This is

what Equation 12-2 calculates. The linear range, in centimeters, is easily derived from the thickness range by dividing the thickness range by the density of the absorber, expressed in milligrams per cubic centimeter. The value of the thickness range is seen to be dependent only on the initial alpha particle energy, in MeV, and the mass number, A, of the absorbing element. Table 12-1 shows both the thickness ranges and linear ranges for a number of common materials. Several gases are grouped first, and water is included in the solid element list in order to compare this very common substance with the light elements. For a given alpha particle, energy, such as 5.15 MeV for plutonium-239, the only variable in the calculation is the mass number. This is why the thickness range increases as the mass number increases. In other words, it takes a greater mass of aluminum than of helium to stop a 5.15 MeV alpha particle.

The range numbers in Table 12-1 illustrate two interesting aspects of alpha particle absorption. First, when considering the thickness ranges, it is clear that, as Equation 12-2 predicts, it takes a greater thickness of an absorber to stop an alpha particle as the absorber mass number increases. Thus only 3.21 mg/cm² of helium is needed to stop the 5.15 MeV alpha particle from plutonium-239, while 12.5 mg/cm² of plutonium is required to stop its own alpha particle. The linear range value changes in a more erratic manner with increasing mass number because the densities of the materials shown in Table 12-1 do not change in a regular fashion as the mass number increases.

Table 12-1.
Ranges of Plutonium-239 Alpha Particles (5.15 MeV)

Absorber	A	Thickness Range (mg/cm^2)	Linear Range (mm)
Hydrogen	1	2.02	225
Helium	4	3.21	181
Nitrogen	14	4.87	39.0
Oxygen	16	5.09	35.7
Argon	40	6.91	39.3
Beryllium	9	4.21	0.025
Water	14.4	4.36	0.044
Skin	12	4.63	0.046
Aluminum	27	6.07	0.022
Silicon	28	6.14	0.025
Iron	56	7.72	0.0099
Copper	64	8.09	0.0090
Zinc	65	8.13	0.011
Germanium	73	8.45	0.016
Platinum	195	11.7	0.0055
Plutonium	239	12.5	0.0063

Detection of Alpha Particles

Nearly all methods for the detection of an alpha particle are based on the ionization created by a particle's passage through matter. The minute quantity of energy released by this ionization can be converted into a tiny flash of light or into an electrical voltage pulse, depending upon the material through which the alpha particle passes. Thus, alpha particles can create faint light flashes, called "scintillations" in materials, or they can create a small electrical signal. Modern scintillation techniques employ photomultiplier tubes, which convert the light flash to an electrical voltage pulse. The ionization methods depend on measuring the electrical pulse created in a gas or a solid (silicon) by the passage of the alpha particle.

Scintillation Detection Methods

One of the earliest methods to detect alpha particles was the use of thin films of zinc sulfide. When an alpha particle strikes this material, it creates a tiny flash of light. This can be observed in a darkened room by using a microscope of low or medium power. This method was difficult to use for the quantitative measurement of alpha particle emission rates but contributed greatly to the development of the laws of radioactive decay. By measuring the time between successive light flashes, it was possible to construct tables that showed the time interval between successive flashes and the frequency of flashes in each time interval. When these data were plotted as frequency versus time interval, it was found that the distribution of events versus time corresponded to the

Poisson distribution (named after S. Poisson, French mathematician in the nineteenth century). The curve is skewed towards the left, which is typical for small numbers of events less than several hundred. For larger numbers of events, this distribution merges into the well-known Gaussian distribution, which is a symmetrical bell-shaped curve. This discovery was important in the recognition that the number of disintegrations per minute in a sample of a radioactive isotope is proportional to the number of those atoms present at a given time:

$$\text{disintegration rate} = dN/dt = -\lambda N. \qquad (12\text{-}2)$$

N is the number of atoms and $\lambda = 0.693/T_{1/2}$ where $T_{1/1}$ is the half-life of the collection of atoms.

Because of the tedious difficulty of using zinc sulfide coatings for the detection of alpha particles, this method was supplanted by others that were based on the detection of the electrical pulse created by ionization in various gases. Other solid materials that create light flashes by the absorption of alpha particles include diamonds.

Modern detection methods, however, still include scintillation techniques that were first developed for the detection and measurement of beta particles of very low energy, such as those from carbon-14 or tritium (hydrogen-3). These methods are also easily applied to the detection of alpha particles with much greater energies. They are based on the use of organic compounds that create a tiny flash of light when activated by an ionizing particle such as an alpha or beta particle. The scintillation compound is dissolved in an organic solvent such as toluene or xylene to which the

radioactive material, in this case plutonium, is added. The organic scintillator solution also contains a "solubilizer" that allows an aqueous plutonium sample to dissolve in the organic mixture, often called a "cocktail", so that the plutonium is evenly dispersed through the cocktail. The mixture, which amounts to about 20 ml, is placed in a glass vial, and the light flashes are detected by a photomultiplier tube in a darkened enclosure. This modern "liquid scintillation detector" can measure disintegration rates accurately up to several million disintegrations per minute (d/m).

When liquid scintillation techniques are used, the measurement of the alpha particle activity is a relatively simple task for plutonium materials in solution. This is because the method usually eliminates any preparatory sample manipulations; the sample aliquot is simply added directly to the scintillator cocktail in the vial and mixed by vigorous shaking. This method, however, can lead to the accumulation of radioactive cocktail residues that may create significant waste disposal problems. The precision and accuracy of the alpha particle activity is probably as good as can be achieved by the use of gas ionization methods, to be described next.

Gas Ionization Methods

The use of ionization chambers to detect alpha particles is nearly as old as scintillation detection methods. It was preceded by the used of "electroscope" measuring devices, which depended on observing the mutual deflection between two very thin gold metal leaves that were attached to a the same electrode. An ionizing source, such as an alpha-particle emitting element like

polonium, would induce an electrical charge on the electrode and would be distributed on both gold leaves so that they repelled on another. This method was just as tedious for quantitative measurements as was the use of the zinc sulfide screen and microscope combination.

During the first decade of the twentieth century, workers in Rutherford's laboratory in England realized that the ionization produced by an alpha particle in a gas could be detected if the ionization took place between two electrodes, one having a positive charge and the other a negative charge. If the voltage difference between the electrodes was sufficiently large, the electrons produced in the gas by the ionizing alpha particle would be quickly attracted to the positive electrode, creating a small electrical pulse. The more massive positive ion of the gas would, of course, move more slowly to the negative electrode. This development led to a family of detection instruments based on the production of an electrical pulse in a gas. Among these devices are the Geiger-Miller counter, the ionization chamber, and the proportional chamber, which differ from one another in their physical design and in the voltage applied to the electrodes.

The proportional chamber is a commonly used detection device for measuring alpha particle activity in a very thin dry source. This device is also called a proportional counter, an internal proportional counter and a 2-pi counter. The latter two terms mean that the radioactive material is placed inside the chamber, and that the device detects all alpha particles emitted into a space equivalent to half of a sphere, which is a volume described by a solid angle of 2 pi.

The gas used in a proportional chamber is usually methane. Other gases or mixtures of gases can be used, but methane is the gas of choice. The flammability hazard from using methane is essentially nonexistent because the amount of methane required is so low that it cannot be burned even to support a flame in air. The methane is supplied to the chamber through an adjustable inlet valve and exits through a flow meter that will measure low flow velocities. For reproducible operation, the chamber must be operated at low methane flow rates in order to avoid internal gas turbulence, which can result in erratic count rates that are usually lower than those observed under proper operating conditions.

The direct current (dc) voltage for a proportional chamber is usually between 2000 and 3000 volts. The main factor that affects the operating voltage is the diameter of the wire that forms the positive electrode that collects the electrons formed in the methane from the passage of each alpha particle. This electrode is usually in the form of a small circular loop, about 1 cm. in diameter. Typical wire diameters are 3 to 5 thousandths of an inch (mils), and the wire is usually gold-coated to resist corrosion from products formed in the ionization of the methane. The positive molecular ions from each ion pair are swept to the metal walls of the chamber, which furnish the negative, or ground electrode of the operating system. The interior dimensions of a proportional chamber for alpha particle detection are such that the walls of the chamber are about 3 to 5 cm from the collecting electrode loop.

Proportional chambers for alpha particle counting can achieve very high precision when operated under stable conditions. A counting precision of less than 0.2% relative

standard deviation can be obtained for repeated measurements of the same alpha particle source. Day-to-day precisions of this level can also be maintained provided a very stable power supply is available for the dc voltage to the collecting loop electrode.

There is a modification of the proportional chamber known as the Frisch grid proportional chamber. This design employs a grid of fine wires that are spaced at intervals of several millimeters and placed horizontally between the alpha particle source and the collecting electrode, which may be a small, circular, horizontal metal plate. The interior dimensions of the chamber are large enough that every alpha particle will expend its energy in the gas before meeting either the walls or the grid. This ensures that the energy of each alpha particle can be measured accurately as well as detected. The Frisch grid is useful for alpha particle sources that contain two or more alpha-particle-emitting nuclides so that the different alpha particle energies of each nuclide can be distinguished.

Solid-State Methods

An offshoot of the developing transistor technology in the 1960s was the discovery that extremely pure silicon wafers can be used as charged particle detectors. Silicon that contains essentially no other chemical element impurities behaves much like the methane gas in a proportional chamber. When a small dc voltage of the correct polarity is placed on one side of the silicon crystal, a region close to the detecting side of the crystal is created that will not conduct an electrical current. This is called the "depletion region". It is usually no thicker than 0.050 mm. The penetration of this

region by a charged particle such as an alpha particle creates a path of electron-hole pairs, analogous to the ion pairs produced in a gas. In this case, the pair consists of a free electron and the "hole" it left when the electron is ejected by the moving alpha particle. The linear range of an alpha particle in silicon is much shorter than in a gas. For an alpha particle whose energy is 5 to 6 MeV this range is only about 0.025 mm. A silicon detector thus has the advantage of being quite thin. Another advantage is the large number of electron-hole pairs produced by an alpha particle in silicon. This number is twelve times that produced in air or methane since it takes only a 2.9 eV energy loss by the alpha particle to create an electron-hole pair in silicon. In methane, this number is 35 eV. In other words, a 5.15 MeV alpha particle from Pu-239 will create 1,870,000 electron-hole pairs in silicon as compared to 156,000 ion pairs in methane. This significant increase in the number of interactions means that the precision of measuring the energy deposited in the silicon by the alpha particle is much greater than the precision attainable in a methane proportional chamber. This becomes important in alpha particle spectrometry, where two or more alpha-emitting nuclides are identified by their different alpha particle energies.

These silicon detectors can be used for nearly any charged particle detection. They are known as silicon surface barrier detectors because of their design and the way they function. Their appearance is like a short cylinder with a diameter between 1 and 3 cm, with an coaxial cable connection on the back side that provides the detector voltage connection. The exterior of the detector is electrically connected to the ground wire of the cable connector and to the front side of

the silicon wafer by means of a very thin gold metal coating. The detectors are provided in a variety of sizes that are determined by the area of sensitive detector surface, and these sizes vary from about 25 mm^2 to more than 500 mm^2. The small detectors are used in alpha particle spectrometry when the highest possible spectral resolution is required. The large detectors are mostly used where higher detection efficiencies are needed, at the expense of poorer energy resolution.

Gamma Rays

Origin of Plutonium Gamma Rays

Gamma ray emission almost always accompanies alpha or beta particle emission from a radioactive atom. This is also true in the decay of all of the common plutonium isotopes. With regard to emission rate, however, while all plutonium alpha (or beta) emissions are an integral part of the decay process, not all of these decays are accompanied by gamma rays. Therefore, the gamma ray emission rate from a plutonium isotope is much smaller than the alpha particle emission rate. In the region of easily detectable gamma rays, those above 50 keV in energy, the ratio of gamma rays to alpha particles is roughly 1/1000.

When a radioactive atom decays to its daughter atom, the nucleus of the daughter atom is sometimes left in an "excited" state. This means that a small fraction of the total energy available for decay has not been expended. In most cases, the daughter nucleus moves from its excited state to the "ground" state by the emission of a gamma ray, which changes neither its mass number nor its nuclear charge. Such transitions to the

ground state occur either directly from the excited state or through a succession of lower-energy excited states to the ground state. In most cases, these gamma ray transitions occur in about 10-8 second or less after the alpha particle emission. Technically speaking, the gamma ray emission is not from the decay process of the parent atom but arises from the daughter nucleus.

The number of different gamma ray transitions from a plutonium daughter, which is a uranium nucleus in the case of alpha particle emission, can be fifty or more. The alpha particles associated with the less energetic gamma ray emissions are not detectable because their emission probability is so low, in the range of 10^{-5} or smaller. Gamma ray spectrometry is useful for the detection of gamma rays that are associated with these low-probability alpha particle emissions because it is possible to use more radioactive material to detect the gamma rays than can be used for routine alpha particle spectrometry. This capability is helpful in identifying the different plutonium isotopes in a mixture, provided enough plutonium material is available for the measurement.

Interaction of Gamma Rays with Matter

Unlike alpha particles, gamma rays have no mass, but are purely electromagnetic radiation similar to x-rays, visible light, infrared radiation, and radio waves. Their interaction with matter is through one of several processes that provide an instant-aneous transfer of their energy to the absorbing matter, unlike the gradual transfer of energy to the absorbing matter: by alpha particles. There are three processes by which a gamma ray can transfer its energy to the absorbing matter: (1) the photoelectric

process, (2) the Compton scattering process, and (3) the pair production process.

The photoelectric process results when the gamma ray transfers its total energy to an atom in the surrounding medium in a single event. The name photoelectric stems from the fact that the excited atom returns to its ground state by emitting a flash of light, usually in the far ultraviolet to the visible region of the spectrum.

Compton scattering process is named after Arthur Holly Compton, an American physicist who discovered the process and was awarded the Nobel Prize for the discovery in 1927. Compton scattering of gamma rays occurs when the gamma ray collides with an electron with a resulting change in the gamma ray's path and the partial transfer of energy to the electron. The change in path direction, known as the scattering angle, can vary from less than 1 to 180-degrees. The amount of energy trans-ferred is proportional to the magnitude of the scattering angle, but even for a 180-degree, or back-scattered gamma ray, a fraction of the original energy remains with the scattered gamma ray. There is a precise relationship between the original energy of the gamma ray, the scattering angle, and the energy of the scattered gamma ray.

Pair Production- can occur only if a gamma ray has an energy greater than 1.02 MeV, which is the equivalent energy of the rest masses of two electrons. This interaction can occur only with an atomic nucleus and not with the orbital electrons. The probability of an interaction increases as the gamma ray energy increases above 1.02 MeV. The result of the interaction is the production of a negatively charged electron, the normal kind, and a positively charged

electron, known as a positron. The positron is unstable in normal matter and will quickly undergo an annihilation reaction with a normal electron, which is also destroyed, producing two simultaneous gamma rays, each with energy of 0.511 MeV. This process is rarely, if ever, observed in plutonium gamma ray spectra because of the scarcity of gamma rays with sufficient energy.

Detection of Plutonium Gamma Rays

As mentioned earlier, the gamma ray activity of plutonium of the weapon grade variety is perhaps a thousand times less that its corresponding alpha particle activity. Because of this, alpha activity measurement is the preferred method for determining the quantity of plutonium when radioactive counting methods are employed. There are, however, several types of plutonium materials where gamma ray measurement is superior to alpha particle activity measure-ments. One is in the measurement of the impurity Am-241 that grows into plutonium materials through the beta particle decay of the short-lived Pu-241 isotope. The other is in the measurement of the relative isotope ratios of Pu-238, Pu-239, Pu-240, and Pu-241 in reactor produced plutonium. There are two detection methods available: (1) sodium iodide scintillation detection, and (2) high-purity germanium single-crystal detection.

Sodium Iodide Scintillation Detectors

Sodium Iodide Scintillation

Detectors are based on the interaction of gamma rays with materials that produce a tiny flash of light when they absorb gamma rays, in a similar fashion to the liquid

scintillators described earlier for alpha particle detection. The solid scintillators differ from the liquid scintillators in that the plutonium material is not dispersed in the scintillation medium, but is external to it. The encapsulation of the solid scintillating material, in this case a single crystal of sodium iodide containing a small amount of thallium, prevents the alpha particle from entering the crystal, and only the gamma rays can penetrate this encapsulation. The sodium iodide is usually in the shape of a cylinder encapsulated in an airtight can of thin aluminum on the bottom and sides, and a clear glass window on the top. Gamma rays that penetrate the encapsulation interact with the sodium iodide by one of the three processes described earlier. The resulting light flash is produced in the sodium iodide by the interaction, a photoelectric process in most cases for plutonium. This light flash is in turn detected by a photomultiplier tube attached to the glass window, and the event is measured and recorded by the proper electronic equipment. Light flashes from very energetic gamma rays may be in the far ultraviolet region, and the photomultiplier is not very sensitive to these. The thallium impurity is added to shift the their flashes to longer and more easily detectable wavelengths.

Both gross gamma counting and gamma ray spectrometry, which measures not only the occurrence of a gamma ray but also its energy, can be accomplished with sodium iodide crystal detectors. The resolution of gamma rays with sodium iodide is inferior to detection with germanium crystal detectors. This may cause two gamma rays of slightly different energies to be indistinguishable from one another although they might be distinguished separately by a germanium detector. Nevertheless, sodium iodide detectors are cheaper than germanium detectors and can be obtained in relatively large sizes, which gives them an advantage of higher efficiency and more suitability for low gamma ray emission rates.

Germanium Detectors

Germanium detectors are made from large single crystals of germanium. They operate in a similar fashion to the silicon surface barrier detectors that are used for alpha particle detection, except that their depletion regions can be as thick as several centimeters. A gamma ray entering the depletion region undergoes one of the three conversion processes described above. This produces an ionization event in the crystal that is collected at the positive electrode when a dc potential of several hundred volts is applied across the crystal. The electrical pulse created by this event is amplified and shaped for measurement of its amplitude, which is directly proportional to the primary gamma ray energy. Germanium crystals have very good energy resolution of gamma rays whose energies differ by only a small amount. These are the detectors of choice for gamma ray sources, such as plutonium, which emit gamma rays of many different energies over a range of 0.05 to 1.0 MeV. These detectors are expensive, delicate, and must be used and maintained at very low temperature, usually by means of a liquid nitrogen source. Nevertheless, they are the only means available for some applications such as measuring plutonium isotope ratios by gamma ray spectrometry, in cases where mass spectrometric methods cannot be used because of their even greater expense.

Measurement Techniques

Gross Alpha Particle Counting

Gross Alpha Particle Counting is a term used to describe methods to determine the alpha particle count rate of a radioactive source without regard to which radioactive nuclides are responsible for the alpha activity. In other words, gross alpha counting methods measure only the detectable alpha particle emission rate of a source, but do not identify the nuclides in the source.

It is important to distinguish between the detectable emission rate of a source and its true disintegration rate. The commonly used alpha particle detection methods, such as proportional gas chambers and liquid scintillation methods do not detect all of the alpha particles that are emitted by a source. The fraction, A/D, where A is the measured emission rate, usually called the "activity", and D is the true emission rate, is known as the counting efficiency. When this fraction is multiplied by 100, it is known as the geometry. Most proportional gas chambers have geometries of close to 50% because the only alpha particles that can be detected are those that are emitted in any direction between the vertical (upwards into the chamber) and the horizontal. Those alpha particles that are emitted downward into the source's support are absorbed by the support and are not detected. When the source support is a smooth, polished material such as metal or glass, a small fraction of the alpha particles emitted at a very slight downward angle may be reflected back up into the chamber where they are detected. For polished glass supports (counting plates) the geometry is about 50.5% to 50.7%, while for polished platinum counting plates the geometry is about 51.5%. These counting

plates are usually square and are made of thin material. Microscope cover glasses for microscope slides make excellent counting plates.

Liquid scintillation detectors have geometries close to 100% for alpha particles because most of the light flashes in the small vial containing the radioactive cocktail are seen by the photomultiplier tube. In this case, however, each individual counting system must be thoroughly calibrated with known amounts of plutonium in order to achieve accurate measurements.

It is important to minimize the amount of dissolved compounds in the solution aliquot that is placed on the sample counting plate because any dried residue from these salts will act as an absorbing material for the plutonium alpha particles. As a general rule, residues that have a thickness of less than 10 micrograms per square centimeter will not cause a significant decrease in the measured alpha activity. A residue, however, that has a thickness of 200 micrograms per square centimeter may cause an absorption loss of about 5%. The dissolved salt concentration in the sample aliquot placed on the sample counting plate can be controlled somewhat by diluting the original sample with 1 $\underline{M}$ nitric acid. This will, of course, reduce the observed counting rate, which may require an increase in the counting time to obtain a desired total of counts.

After the liquid containing the plutonium has dried on the sample counting plate, the plate is placed in a proportional counting chamber to measure the activity on the plate in terms of counts per minute (c/m). The fine wire loop inside the chamber provides the positive high voltage for collecting the electrons created by each alpha particle

passing through the chamber. Various designs are used for closing the chamber after the sample plate is placed in it. Some consist of a slide-out drawer that forms the bottom of the chamber and that can be raised against a rubber-sealing gasket when the drawer is closed. In other designs, the bottom of the chamber is a separate metal support for the sample plate, hinged vertically so that it can be swung out to place or remove a sample plate. It also must be fitted with a mechanism for raising it against a sealing rubber gasket. The gas outlet should be fitted with a gas flow indicator so that the gas flow can be reduced to a milliliter per minute or so after the closed chamber has been flushed with gas. A gas flow that is too rapid will create a turbulence within the chamber. This may lower the count rate of the sample, resulting in erroneous measurements.

The correct operating voltage of a proportional chamber is determined by counting the same sample at different voltages, usually on the order of one or two thousand volts, at increments of 50 volts. When a graph is prepared of the count rate as a function of the voltage, a curve known as a "plateau" is generated.

The flat portion of the curve, the plateau, is a region where a change in chamber voltage will not affect the count rate appreciably. This plateau region should generally have a length of 300 to 400 volts and a slope of less than 0.3% per 100 volts. The slight increase in count rate on the plateau is caused by the more efficient detection of back-scattered alpha particles as the voltage increases. A typical operating voltage is about 2/3 of the way along the plateau in the direction of the higher voltages. The shape of the plateau can

change over time from the deposition of polymerized gas impurities on the loop electrode.

Alpha Particle Spectrometry

Alpha particle spectrometry makes use of a system that measures not only the amount of alpha particle activity of a sample but the energy of each alpha particle that is detected. In plutonium radiochemistry, it is most often used for the measurement of the amount of Am-241 present in a plutonium sample (through decay of Pu-241), and for the measurement of the fraction of alpha particle activity caused by Pu-238.

Two kinds of detectors can be used. The more common one is the silicon surface barrier detector. It is used for alpha particle sources containing several hundred thousand disintegrations per minute or more. This SSB detector must be used in a small chamber that can be evacuated of air in order to avoid absorption of the alpha particle energy by air molecules before the alpha particles enter the detector. Its detection efficiency is relatively low because its sensitive area intercepts only a small fraction of the alpha particles emitted by the source. Its energy resolution, however, is much superior to that of the Frisch grid chamber. The advantage of the Frisch grid chamber is its relatively high detection efficiency, a little more than 50%. It does not have the high energy resolution of the SSB detector, but in applications with plutonium sources this is not a real disadvantage. The Frisch grid chamber is superior for the measurement of very low alpha activity in environmental samples. Its higher counting efficiency decreases the time required for a desired measurement precision.

In actual use, either detector is connected to an electronic recording system that measures the energy of each electrical pulse from the detector and stores this record of the pulse in a "bin" or channel according to the pulse's energy. At one time, this electronic measuring system was called a "pulse height analyzer". The more modern term is "multi-channel analyzer", or MCA. An MCA is a sophisticated device, useful for the analysis of many kinds of data where detectors produce electrical signals whose amplitudes are proportional to the energies of the detected event. The MCA contains a device known as an "analogue-to-digital (ADC)" converter that changes the amplitude of the incoming signal to a series of very rapid counts whose total number is proportional to the amplitude of the original signal. If the converted signal produces 50 counts, a stored number in the channel 50 box is multiplied by one; if the converted signal produces 100 counts, the number in the channel 100 box is multiplied by one. In a typical MCA, there can be many thousands of storage channels, thus permitting the high resolution required by high-resolution detectors. The accumulated data in all channels can be shown graphically on a video display as the number of events stored in each channel, and this graphical information can be printed. The digital information can also be printed to show the number of stored events in each channel. Regions of interest in the display can also be selected to show the total number of events in the channels included in the various regions of interest. For example, the MCA can be set up to measure the Pu-238 alpha activity automatically in a plutonium source. In this particular application, Am-241 must first be removed from the sample because the alpha particle energy of Pu-238 is very close

to that of Am-241 and cannot be resolved by either the SSB detector or the Frisch grid chamber.

Gamma Ray Spectrometry

Gamma Ray Spectrometry is a tool that can be used to determine the isotope ratios of Pu-238, Pu-239, Pu-240 and Pu-241 in a plutonium source. In this case, a germanium detector is connected to the MCA to measure the gamma rays from the plutonium source. Analysis of this gamma ray spectrum for specific gamma rays from each isotope permits the calculation of the isotope ratios. Gamma ray spectrometry is also useful for the determination of non-plutonium, gamma-ray-emitting impurities in plutonium. The main difference between the application of gamma ray spectrometry and alpha particle spectrometry is the manipulation and maintenance of the two detector systems and the size of the sample required for the particular application.

A germanium gamma ray detector is a bulky thing, mainly because it must be operated at liquid nitrogen temperature (-195°C). The detector itself is small, a right-circular cylinder not more than 5 cm. One end of a long copper rod is attached to its bottom, and the other end of the rod is immersed in large dewar containing liquid nitrogen. The detector and the copper rod are encased in a vacuum-tight housing to prevent condensation of moisture in the air on the detector.

The number of gamma rays emitted by plutonium is much smaller than the number of alpha particles, for a given mass. The gamma-to-alpha ratio for gamma rays more energetic than 50 keV is roughly 1 to 1000. This ratio refers to the total number of all

gamma rays that extend in energy to more than 500 keV. Therefore, for quantitative measurement of the various gamma rays from the plutonium isotopes, a relatively large amount of material is required compared to that for the measurement of alpha particles. Thus, while 1 to 3 micrograms of plutonium is adequate for alpha particle spectrometry, several milligrams is the usual amount required for gamma ray spectrometry.

Most gamma ray spectrometry procedures for determining plutonium isotopic ratios include a preliminary purification to remove Am-241, which has a very abundant gamma ray at 59.6 keV (70% of the alpha emissions are associated with this gamma ray). A solution of the purified plutonium in a 10-ml screw-capped vial is placed near the germanium detector in exactly the same position that was used for the calibration sample containing known ratios of the plutonium isotopes. The gamma rays employed for the isotopic analysis range between 43 and 150 keV. Other higher-energy gamma rays are available, but because they are less abundant, their use requires larger amounts of plutonium. Important factors in the use of this method are the uniformity of the vials, the position and distance of the vials from the germanium detector, the composition of the plutonium solution, and the mass of plutonium in the solution. The relative precision of the measurements for the various isotope ratios is generally less than 0.5%. The accuracy, when compared to results from the more expensive mass spectrometric procedure, are close to 0.3%, except for the Pu-238 ratio, which shows about a 10% lower value for the gamma ray spectrometry procedure. This is a result of U-238 contamination in the mass spectrometric filament materials. For the most precise Pu-238 determination, alpha particle spectrometry is the method of choice.